Production and Characterization of carbon-free bi-functional cathodes for the use in lithium-air batteries with an aqueous alkaline electrolyte

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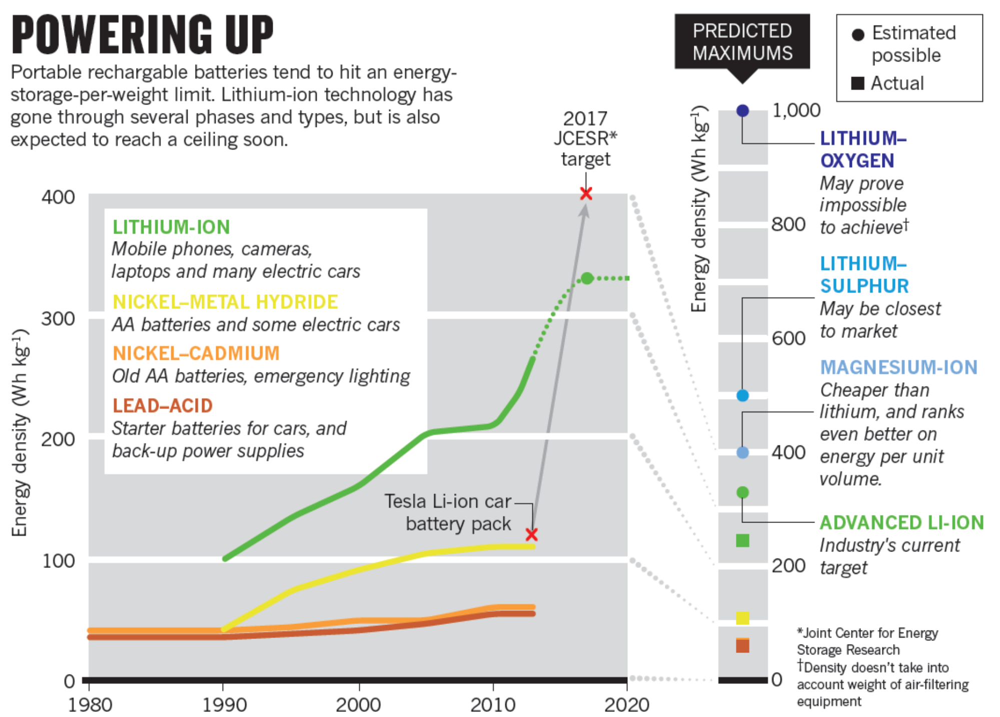
Presentation outline

- Application of EIS in battery research at DLR
  - Motivation Li-air batteries
- Electrode production techniques at the DLR
  - Cathode for the Li-air battery
- Catalyst screening of bifunctional cathodes (ORR and OER)
- Conclusion and outlook

Activities of the „Batterietechnik“ team

Production and Characterisation of cathodes for ***Lithium-Sulfur*** *and* ***Lithium-air batteries***

Characterisation of ***Li-ion batteries*** with in-situ and ex-situ-methods

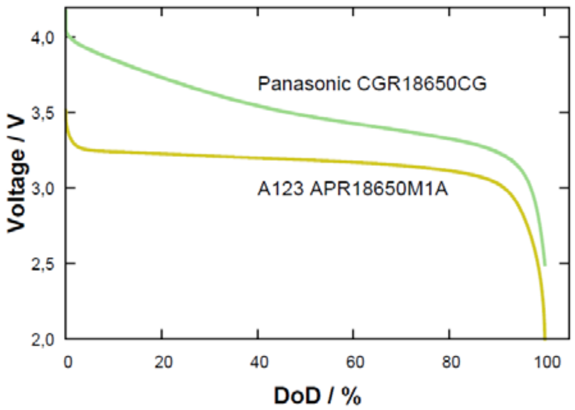


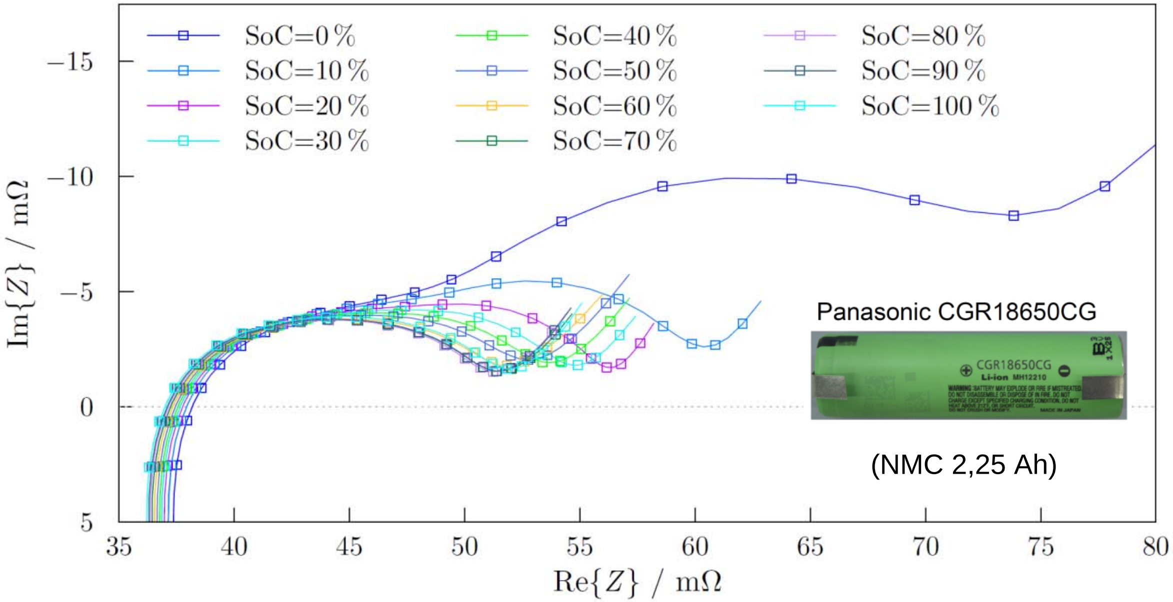
Source: N AT U R E | VO L 5 0 7 | 6 M A R C H 2 0 1 4

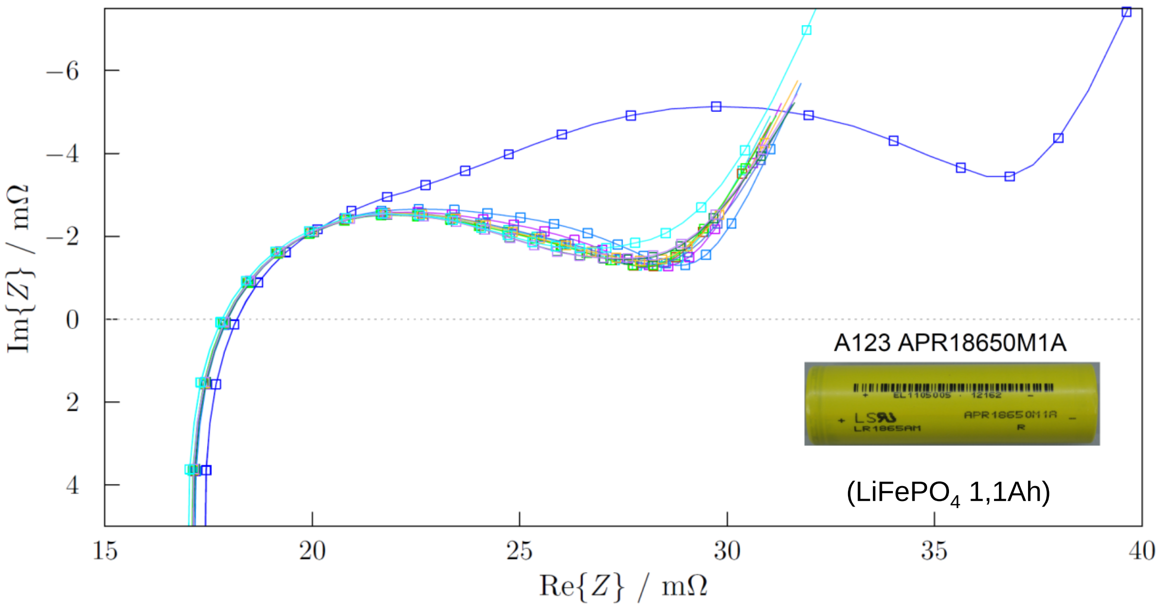
DLR

EIS measurement at different SOC

Discharge at 1C







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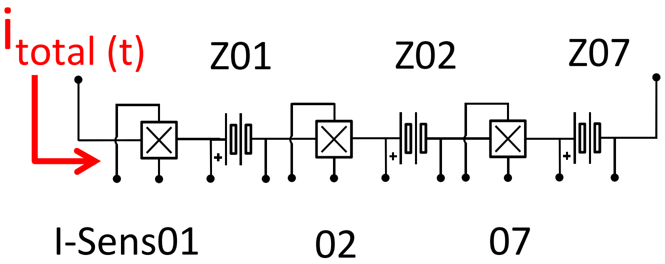
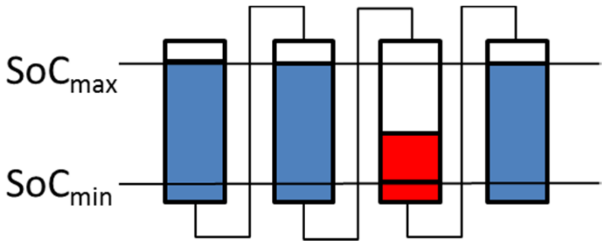
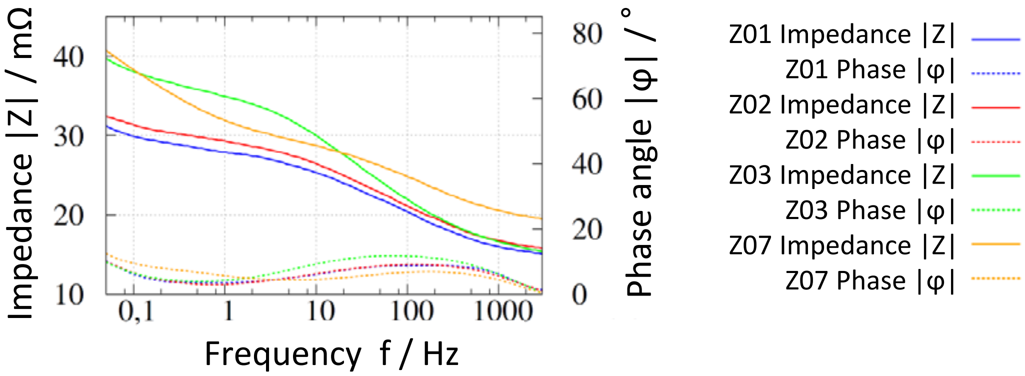
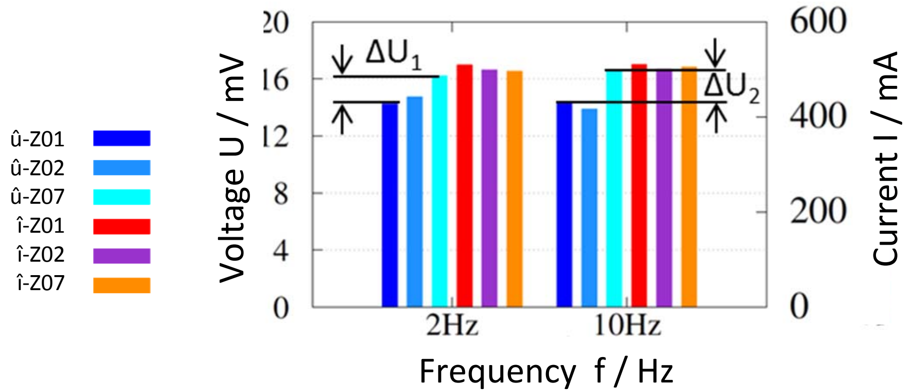
Discrimination of SOC and SOH of serial connected batteries

Serial connection V2		
Z01	U=3,25V	SoH100
Z02	U=3,25V	SoH100
Z07	U=3,25V	SoH60



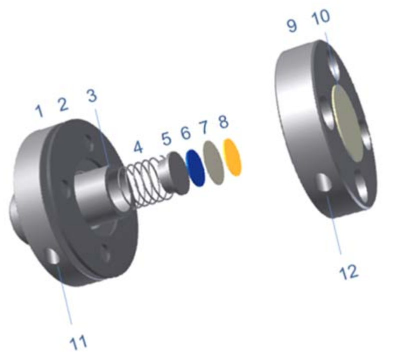


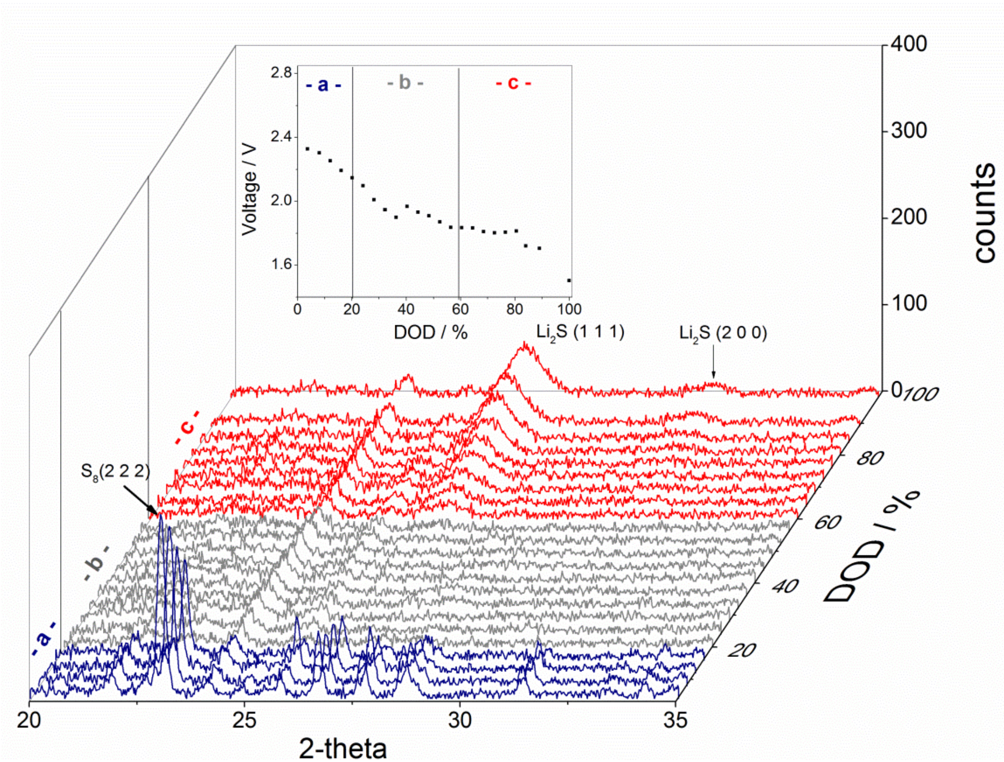


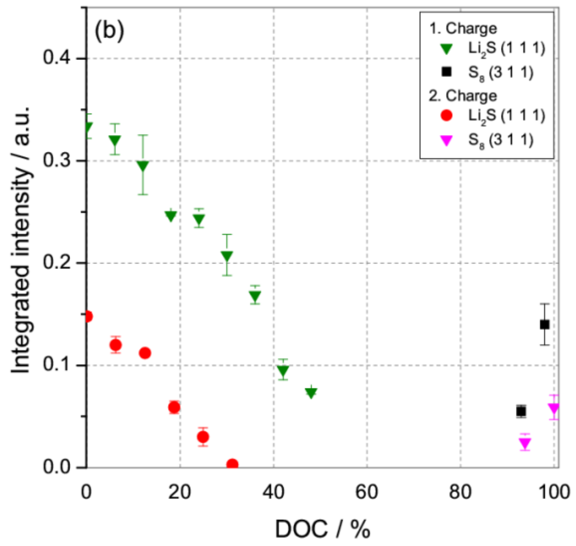


In-situ XRD and EIS measurements during discharging

Li-S batteries







N. A. Cañas, S. Wolf, N. Wagner, K. A. Friedrich. J. of Power Sources, 226 (2013) 313-319.

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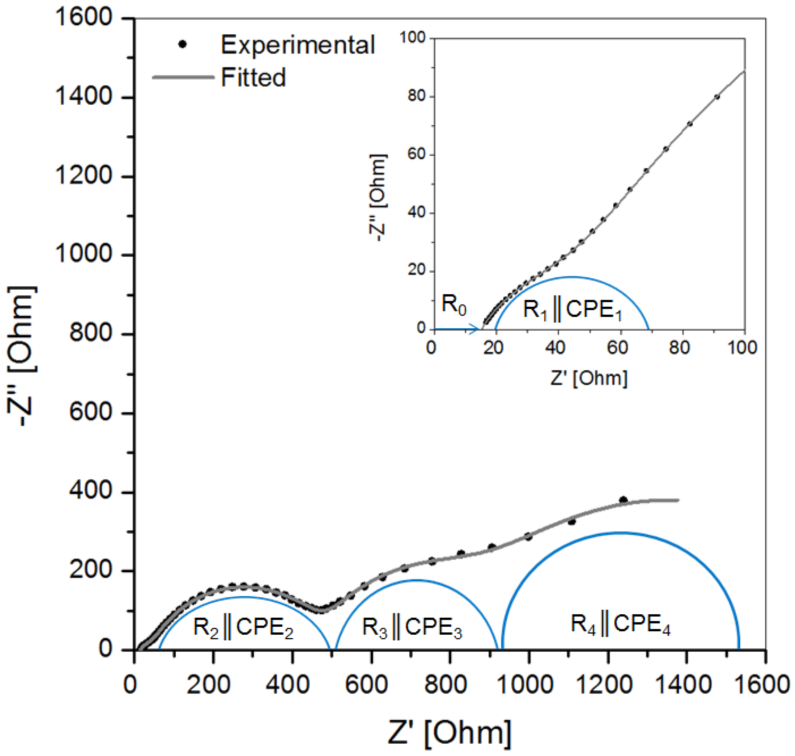
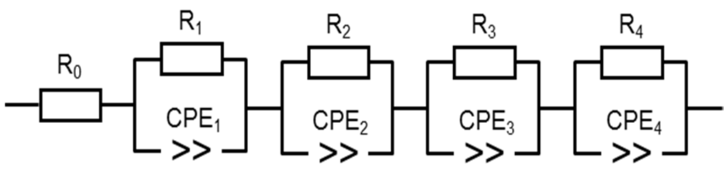
Electrochemical Model of Li-S Battery



Equivalent circuit



Model	Chemical and physical cause
R_0	Ohmic resistance
R_1-CPE_1	Anode charge transfer
R_2-CPE_2	Cathode process: charge transfer of sulfur intermediates
R_3-CPE_3	Cathode process: reaction and formation of S_8 and Li_2S
R_4-CPE_4	Diffusion

Motivation

Why Li-air batteries?

- Highest theoretical specific energy density (11.425 Wh/kg) Cathodic reactant, O_2 from air, does not have to be stored
- Environmental friendliness
- Higher safety than Li-ion batteries

  (only one of the reactants contained in the battery)
- Potentially longer cycle and shelf lives

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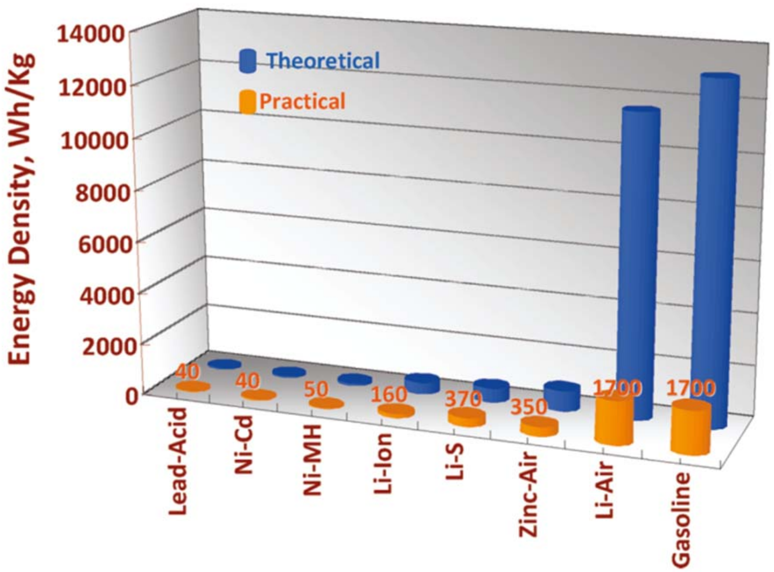
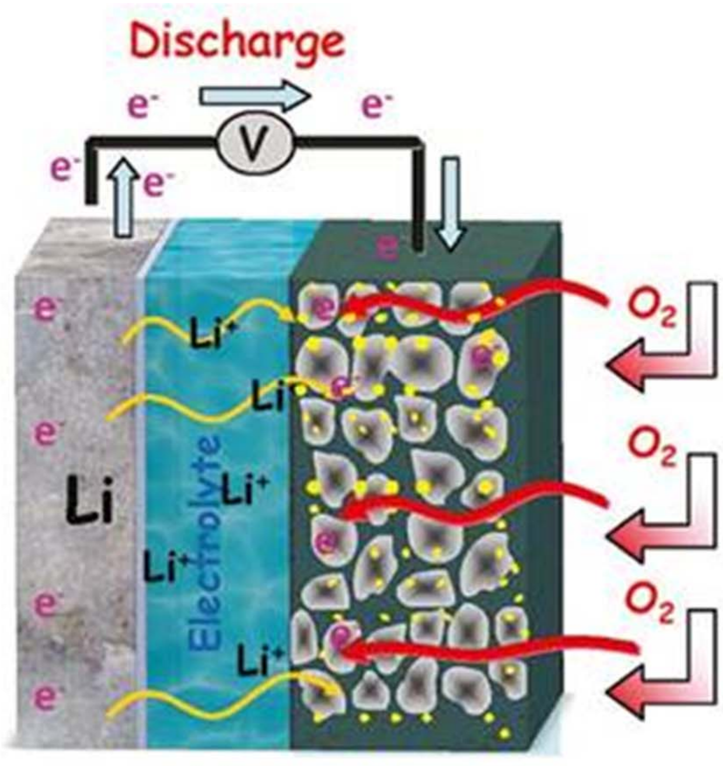
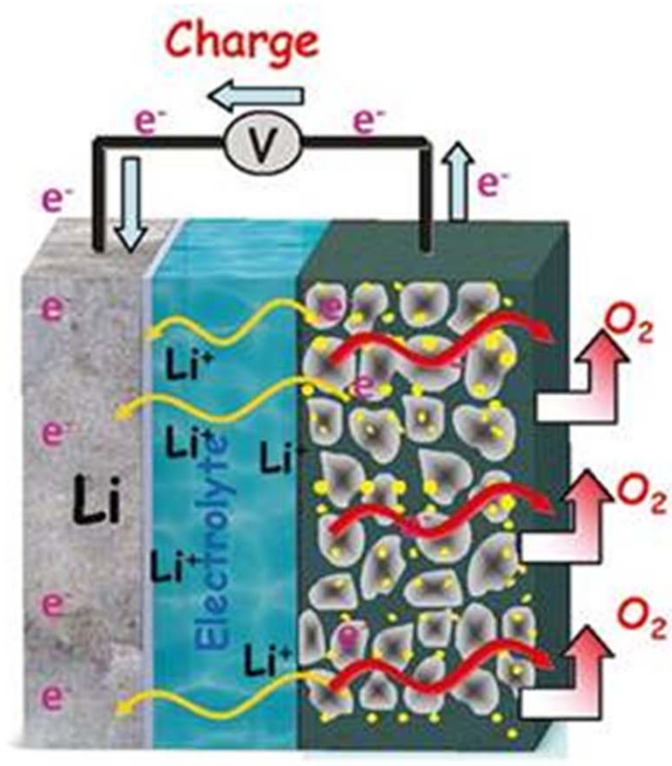


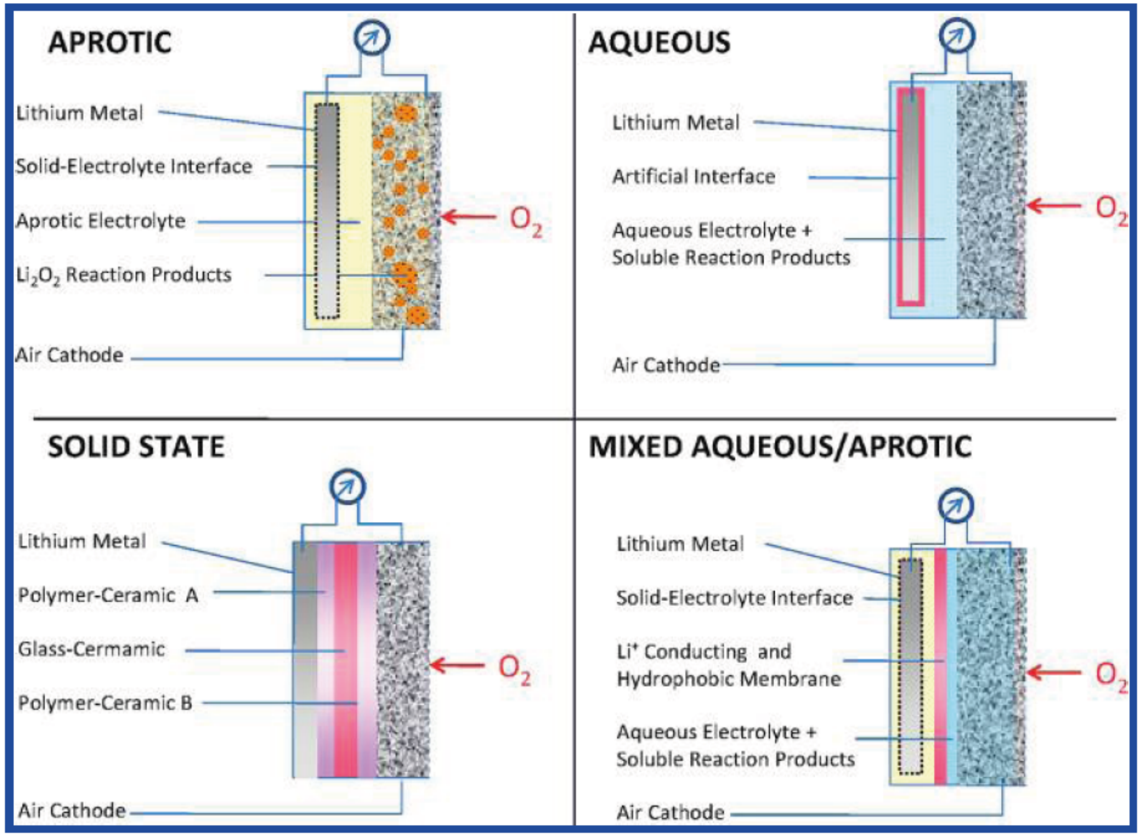
G. Girishkumar et al., J. Phys. Chem. Lett., **2010**, 1, 2193-2203

Schematically representation of a Li-air battery





Architectures of Li-air Batteries



Non-aqueous electrolyte:

$2Li^+ + O_2 + 2e^- \rightleftarrows Li_2O_2$ E_{rev}= 2,959 V

$2Li^+ + 2e^- + (1/2)\, O_2 \rightleftarrows Li_2O$ E_{rev}= 2,913 V

Aqueous electrolyte:

$4Li + O_2 + 2H_2O \rightleftarrows 4LiOH$ (alkaline media) E_{rev}= 3,446 V

$4Li + O_2 + 4H^+ \rightleftarrows 2H_2O + 4Li^+$(acidic media) E_{rev}= 4,274 V

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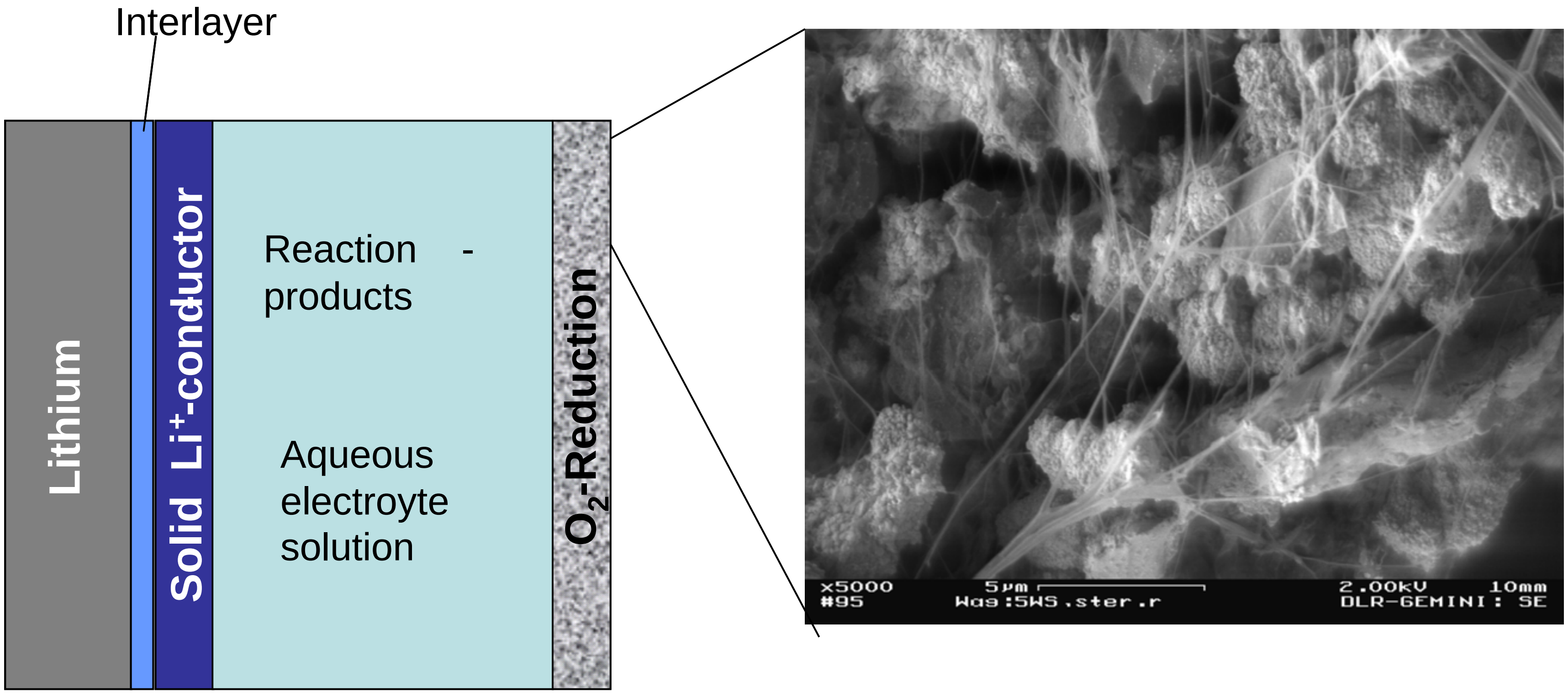
Schematically representation of Lithium-Air Battery with Aqueous Electrolyte



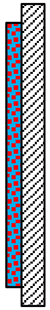
Reaction equation (alkaline Electrolyte):

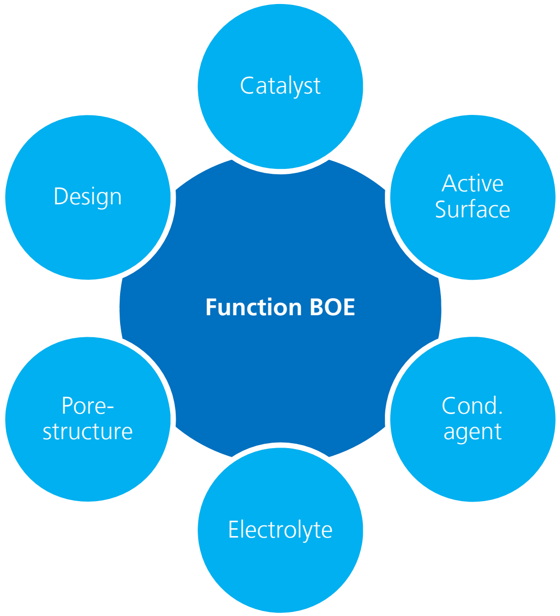
$4\ Li + O_2 + 2H_2O \leftrightarrow 4LiOH$; $E = 3{,}45\ V$

Bi-functional Oxygen-Electrodes: Design

- Bi-functional Oxygen-Electrodes = catalizes ORR and OER

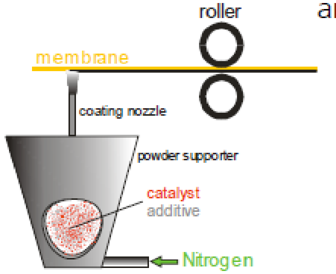
- Depending on manufactoring process every electrode consists of:
    - Catalyst(s)
    - Conductive agent (C, Graphit…)
    - Binder (PTFE, PVdF…)
    - Substrate (Metal mesh,…)



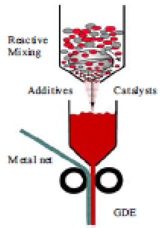


- Different manufactoring processes used at DLR: Dry Powder Spraying, Reactive Rolling an Mixing, Pressing and APS

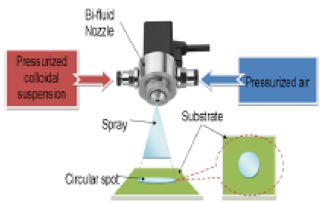
Dry Powder Spraying



Reactive Rolling and Mixing (RMR)



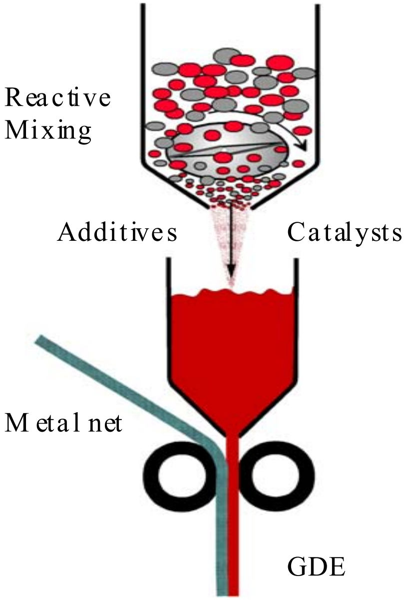
Colloidal Suspension Spraying



Atmospheric Plasma Spraying

Production Techniques

-Dry Spraying Technique
-Wet Spraying Techniquen
- Reactive Mixing
and Rolling (RMR)
-Screen printing
-…



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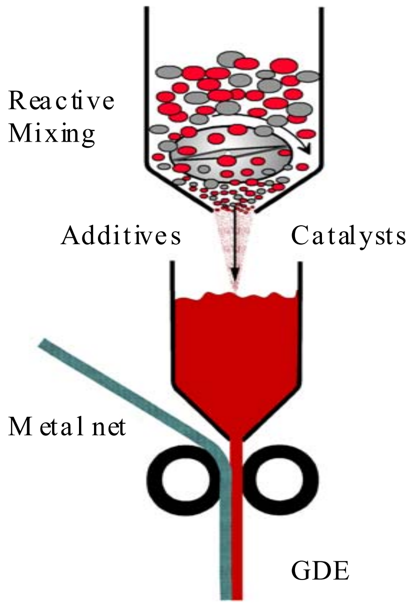
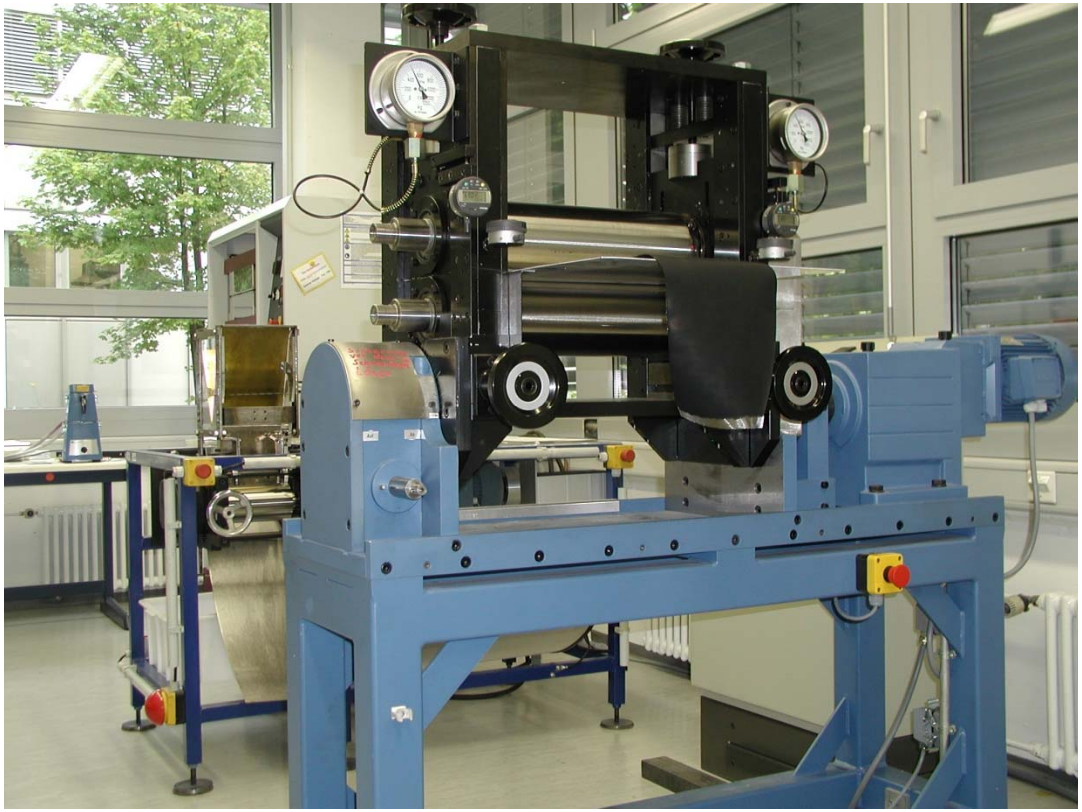
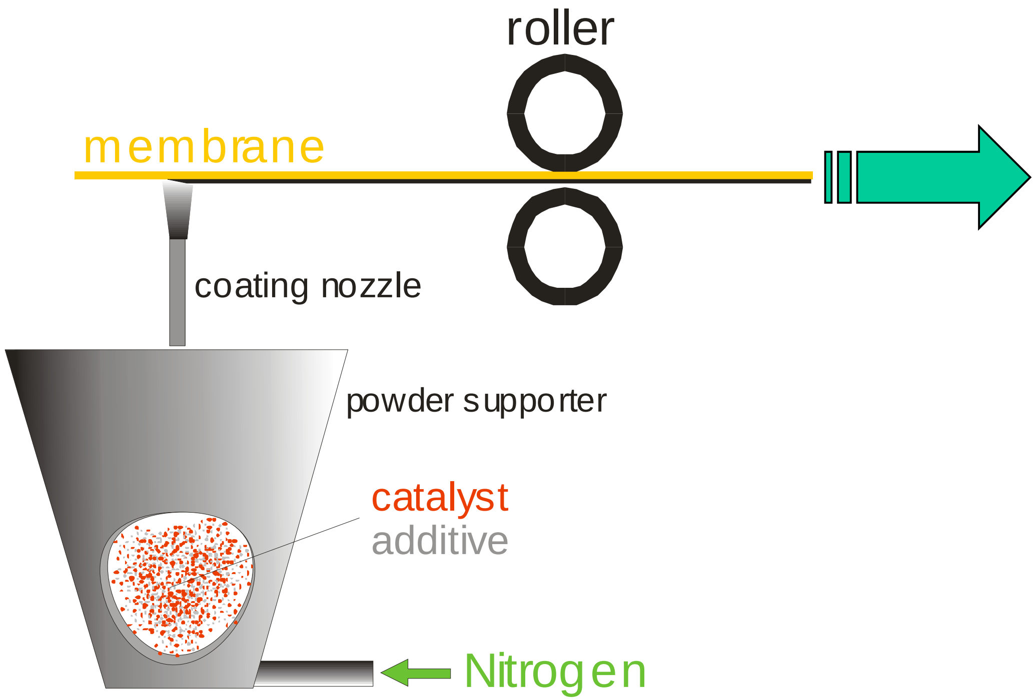
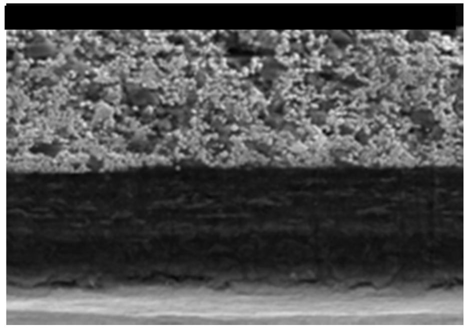




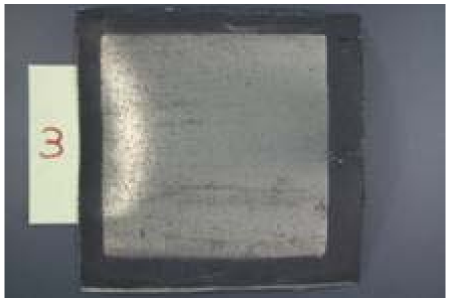
Dry Powder Spraying Technique





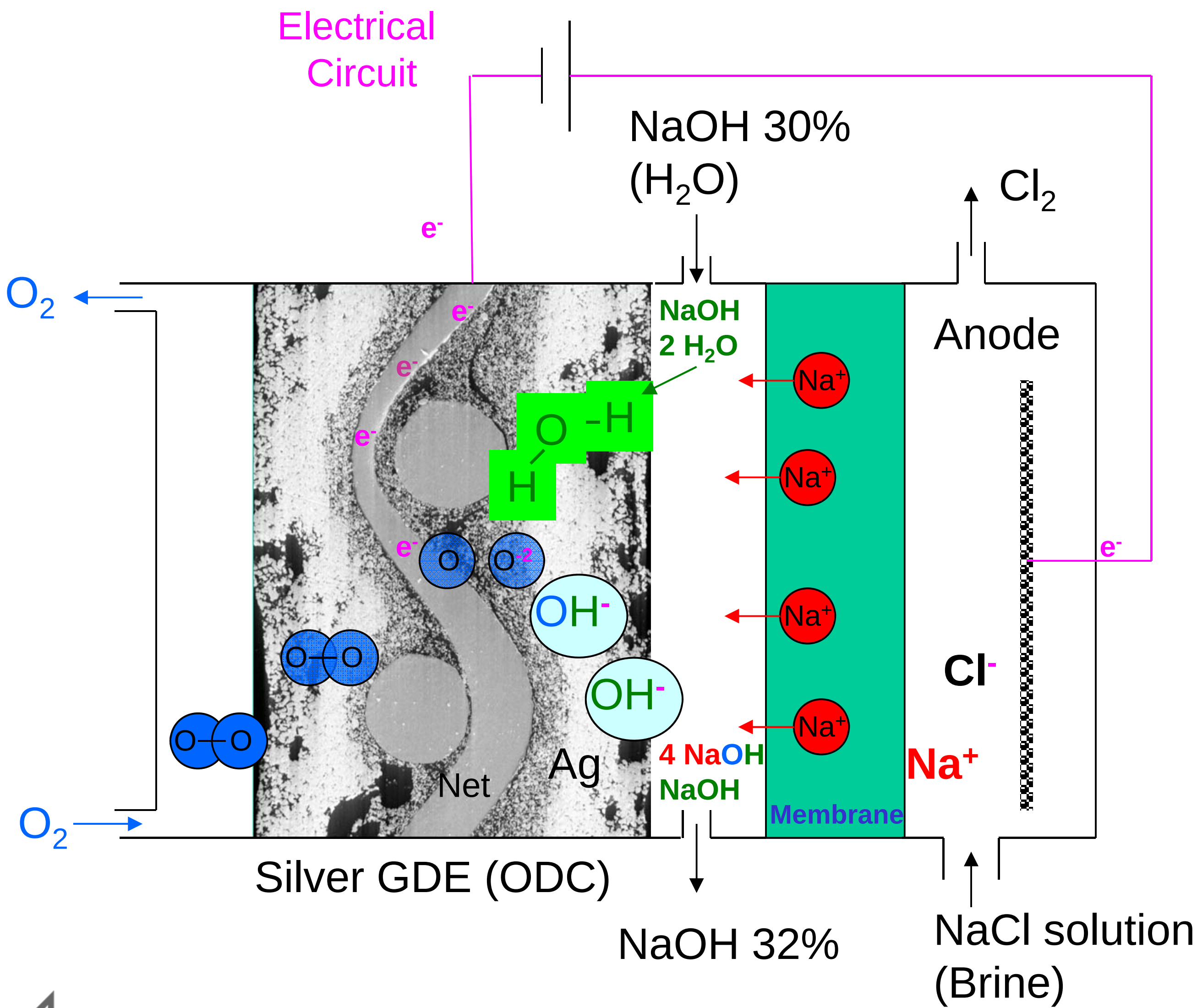
RMR
(Substrat)

Dry sprayed layer



Top view

N. Wagner, T. Kaz, DE 101 12 232 A1, 2002

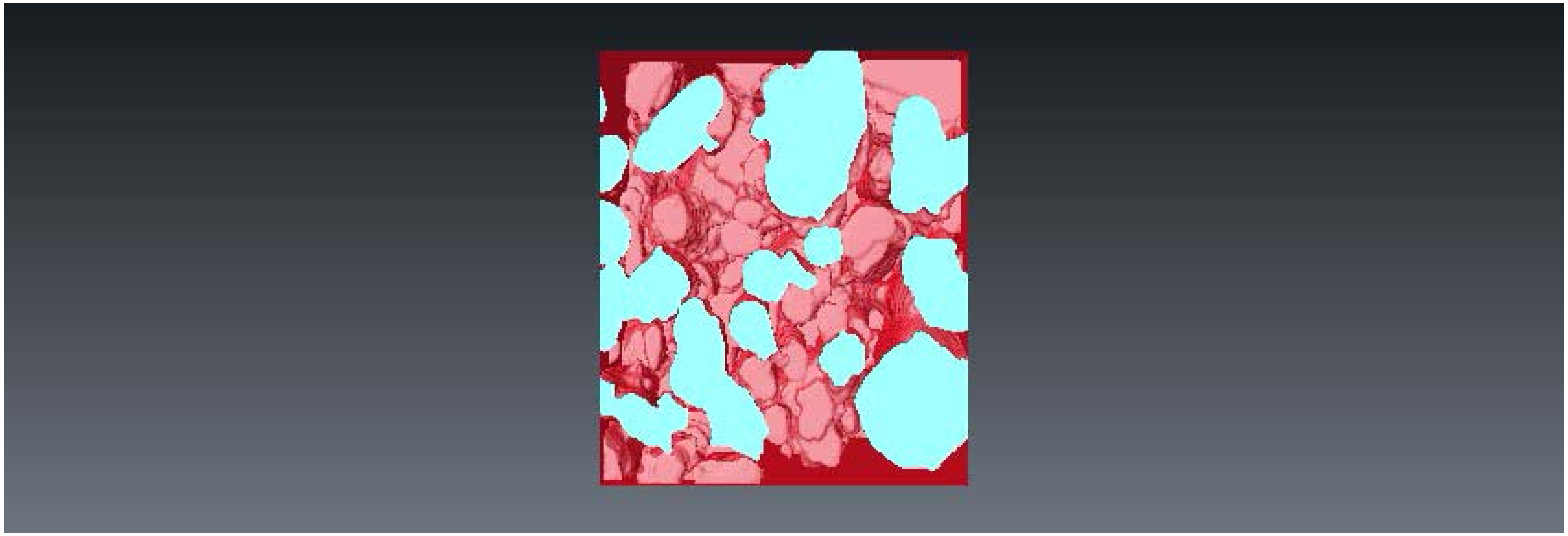

Electrical Circuit
NaOH 30% (H_2O)
Cl_2
e^-
O_2
NaOH
2 H_2O
Anode
Na^+
O -H
H
O
O^{-2}
OH^-
O-O
Cl^-
4 NaOH
NaOH
Net
Ag
Na^+
Membrane
O_2
Silver GDE (ODC)
NaOH 32%
NaCl solution (Brine)

Chlorine production with ODC (Oxygen Depolarised Cathode)

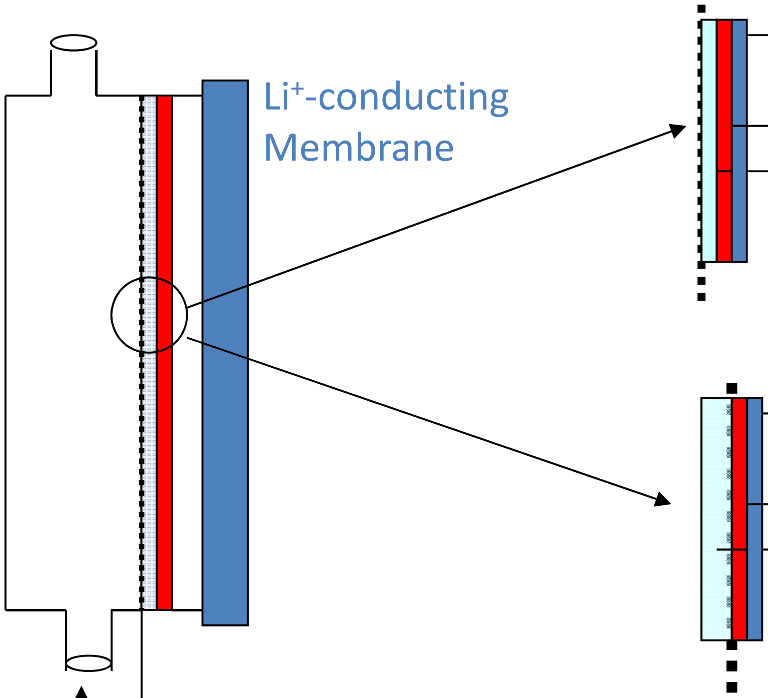
Chlorine production unit with ODC technique at Bayer in Ürdingen (20,000 t/y) since May 2011

CT picture of a Silver gas diffusion electrode

FIB-TEM picture of a Silver gas diffusion electrode



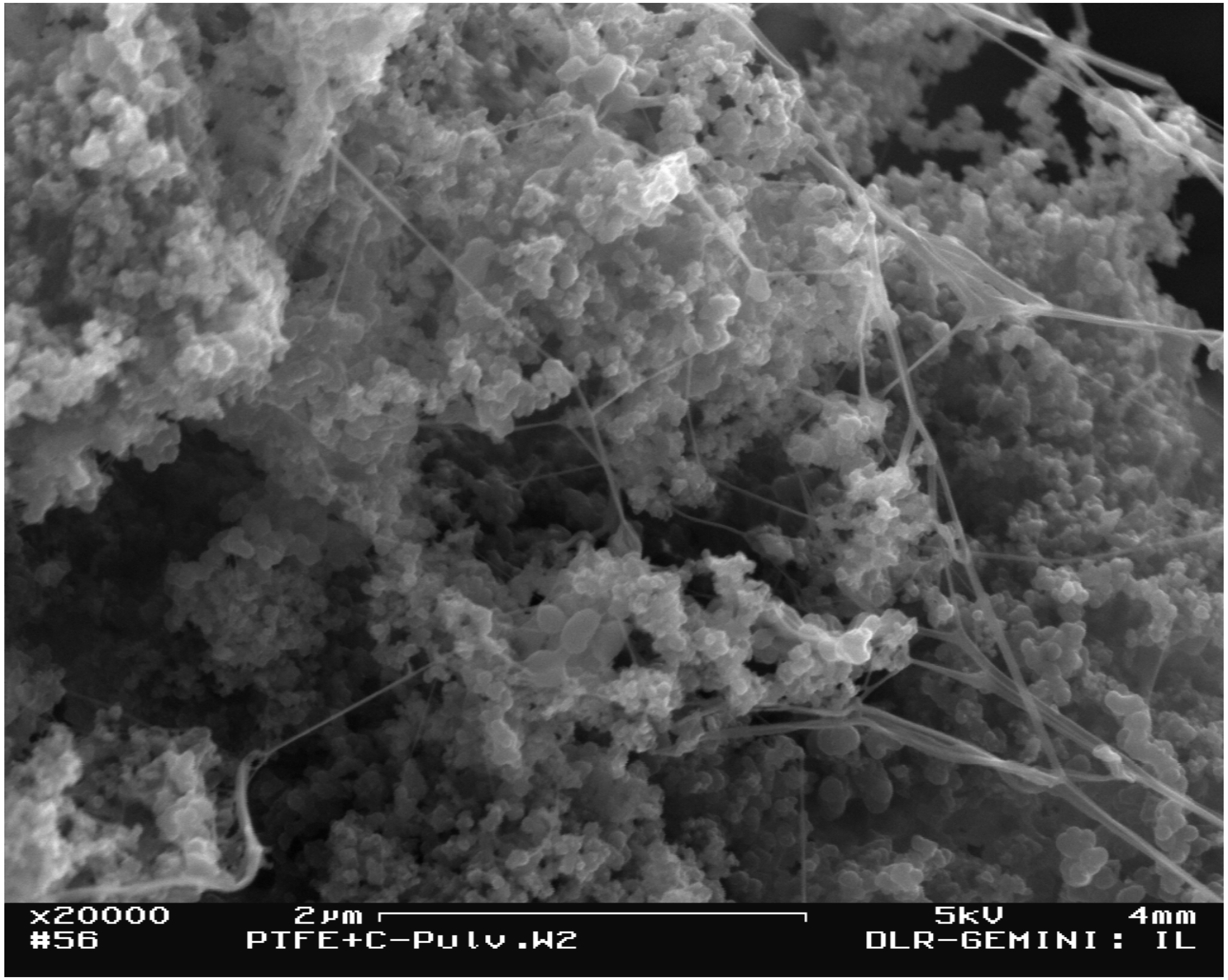
Possible production options for multilayer electrodes



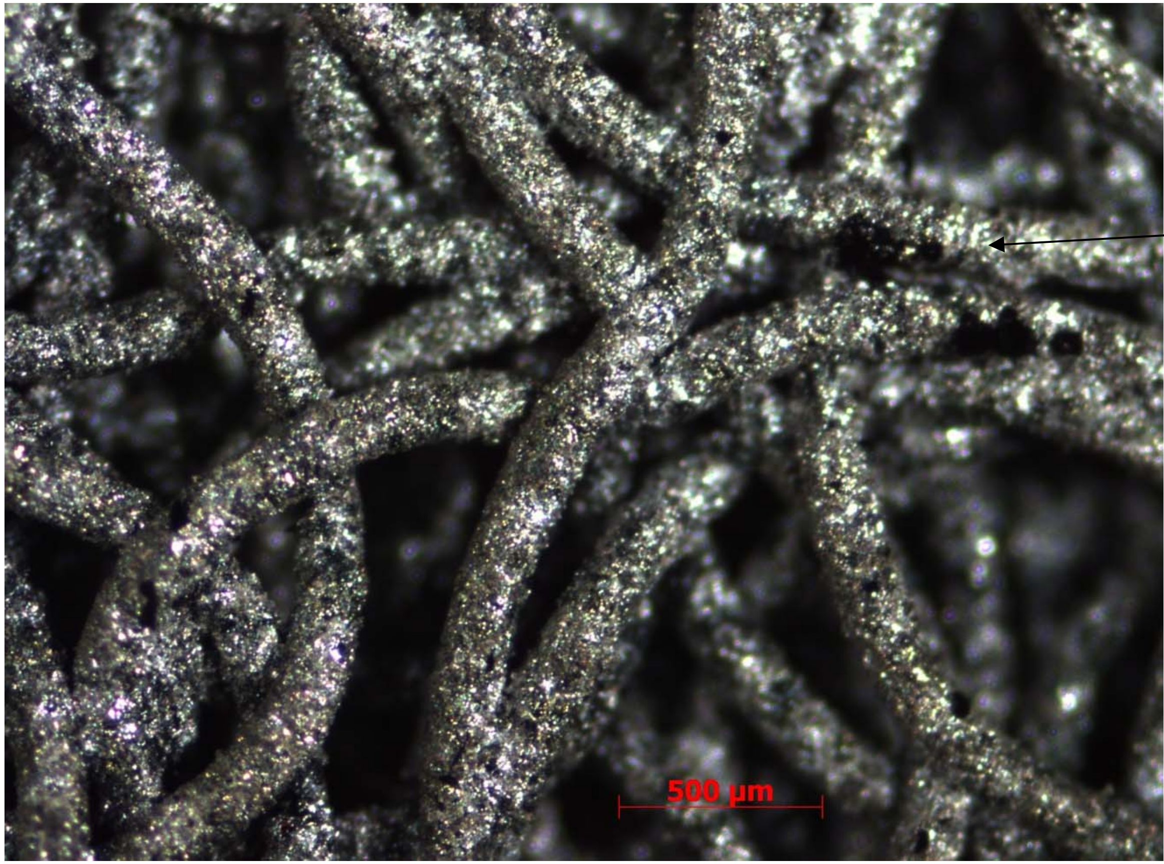
Composition:

- chemical composition (metals and metal oxides)
- structure

PTFE-bounded Carbon Powder: SEM- picture



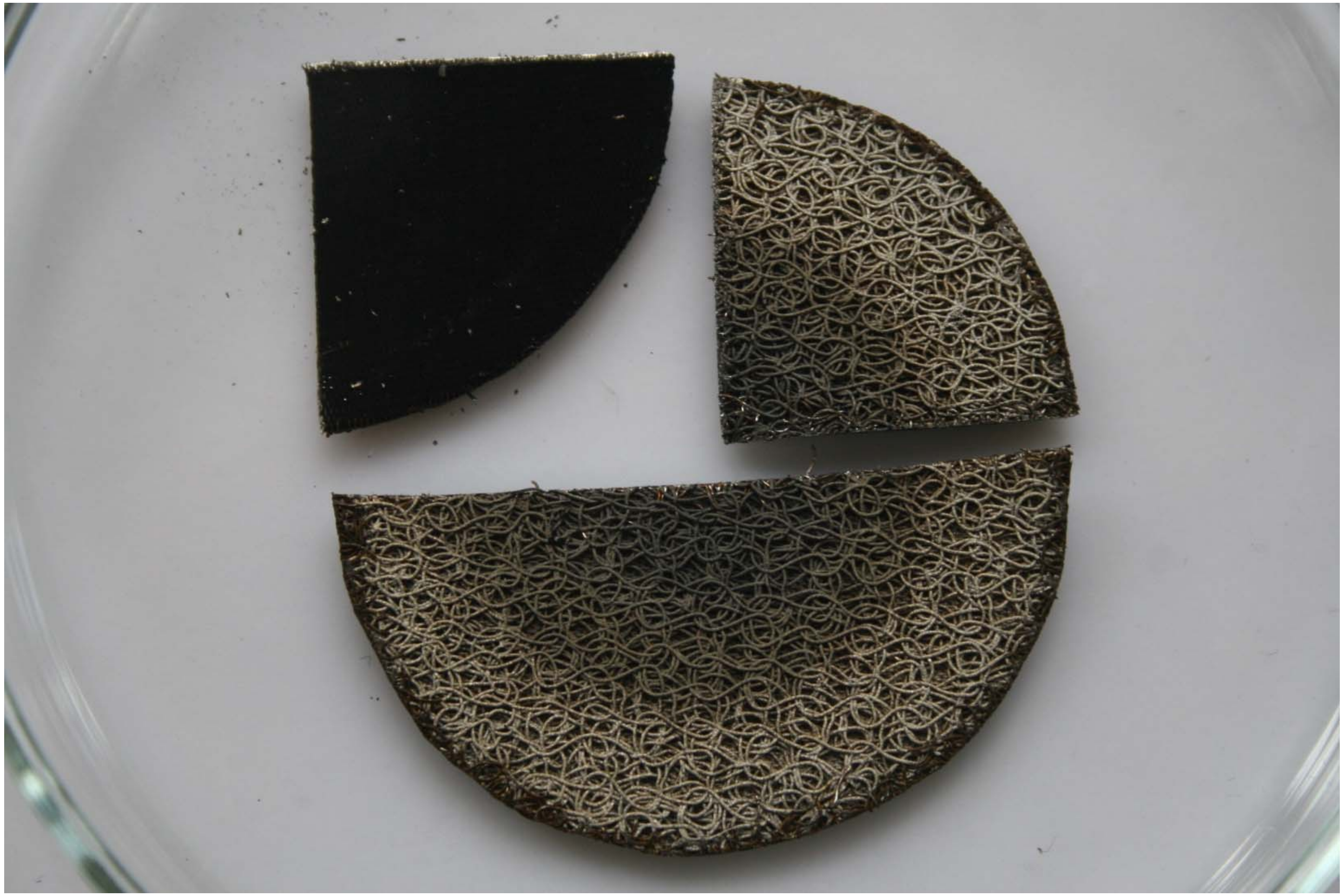
VPS coated cathode for Li-air battery



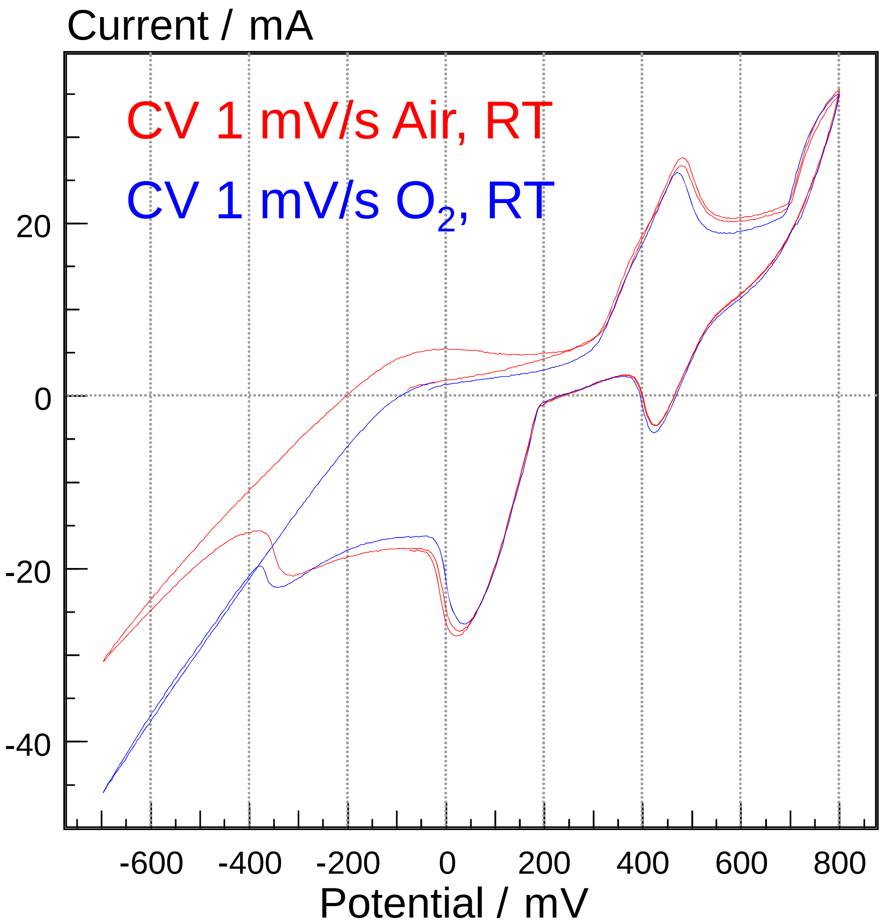
Cro-Fer net
coated one side with
Ag+LSCF
other side with C+PTFE

DLR

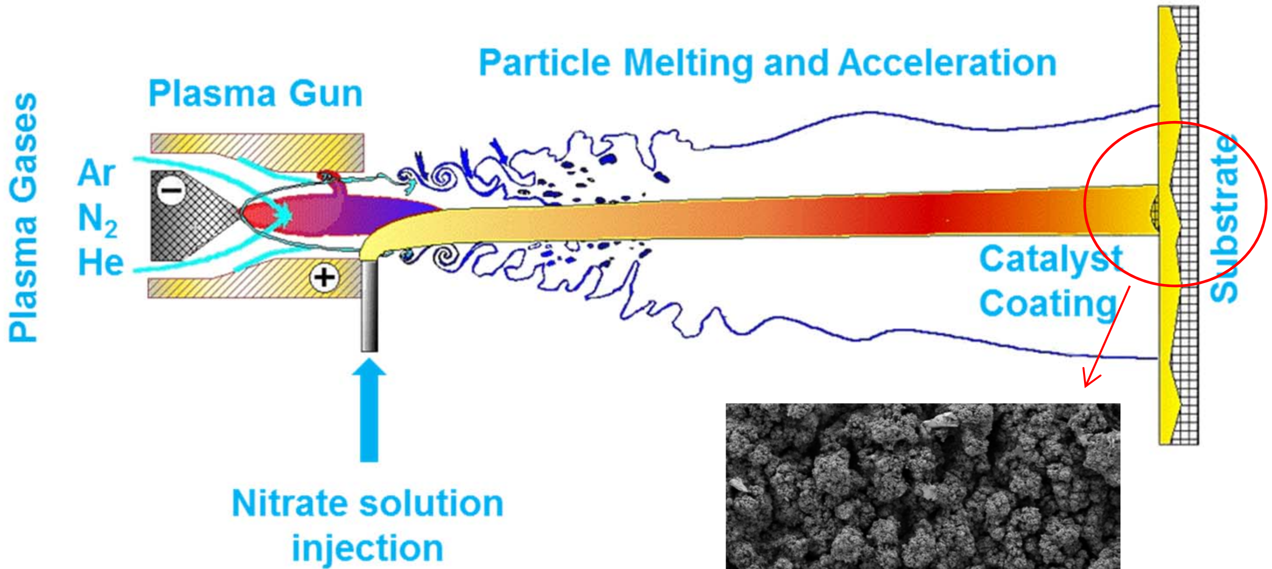
Picture of APS-coated porous substrate with 50 vol. % Ag+50 vol. % LSCF, gas side C/PTFE (dry sprayed)



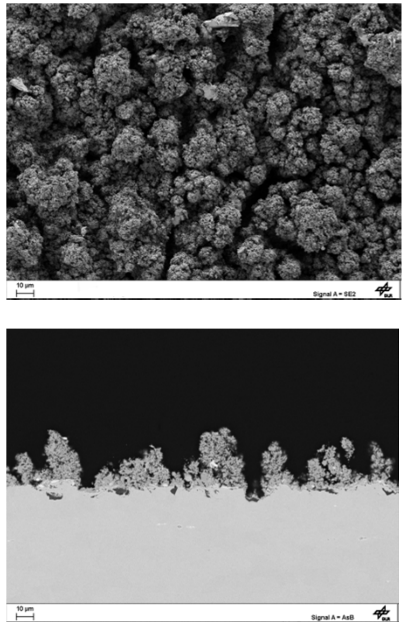
CV: with Ag+LSCF (APS, electrolyte side) and PTFE+C (Dry Powder Spraying, gas side) coated Rhodius-Net in 1 N LiOH, Reference electrode: Hg/HgO



Atmospheric Plasma Spraying (APS)



0.3M
nitrate solution
for injection



SEM of catalyst layer
and cross section
plasma sprayed at DLR

P. Fauchais, J. Phys. D: Appl. Phys. 37 (2004) R86–R108

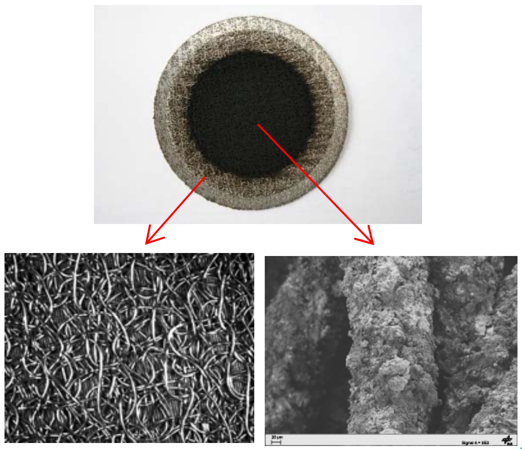
Manufactoring of bifunctional gas diffusion electrodes

Oxide catalysts

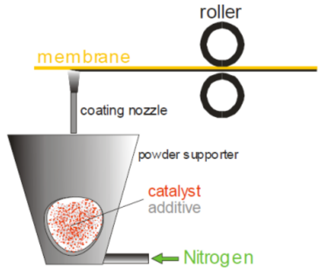
($La_{0.6}Ca_{0.4}CoO_{3...}$) can be sprayed on for example a Rhodius substrate with APS

Catalyst layer

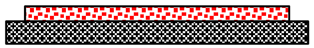
Rhodius substrate



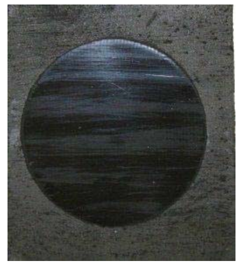
Electrodes with noble metal and other catalysts can be made with dry power spraying technique



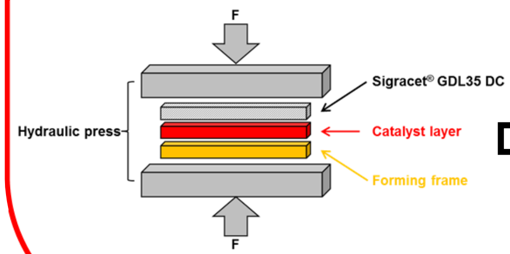
Catalyst layer = catalyst+carbon/ graphite+binder



Graphite GDE substrate



or by pressing the catalyst layer on for example a Sigracet® GDL 35 DC with a hydraulic press



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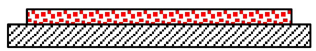
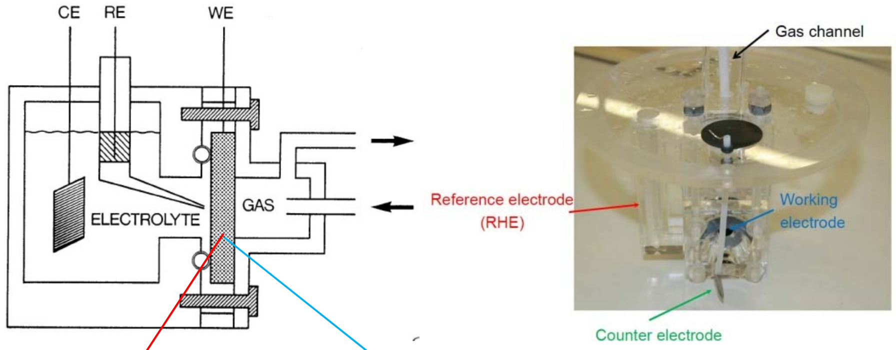


Sigracet® GDL35 DC

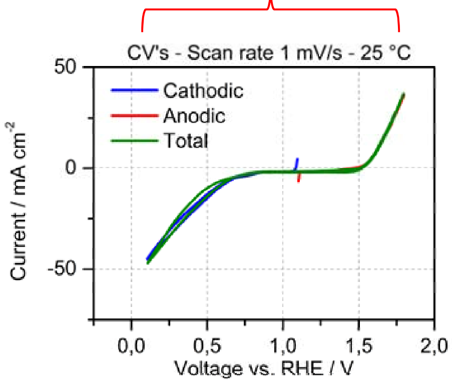
Screening of bifunctional catalysts

Experimental

- Thin catalyst layers reduce the influence of the electrode structure
- Cyclic Voltammetrie was carried out at a half cell with 1M LiOH (aq.) and 25° C and 50° C
- Gas O_2, platinum counter electrode (CE), reversible hydrogen reference electrode (RE)

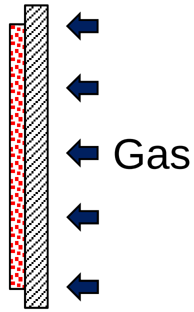


- Potential range 0.1V - 1.8V vs. RHE



Noble metal catalyst configuration

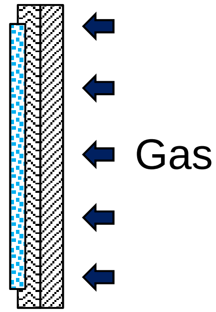
80 wt % graphite + 20 wt % PTFE + catalyst



Electrode

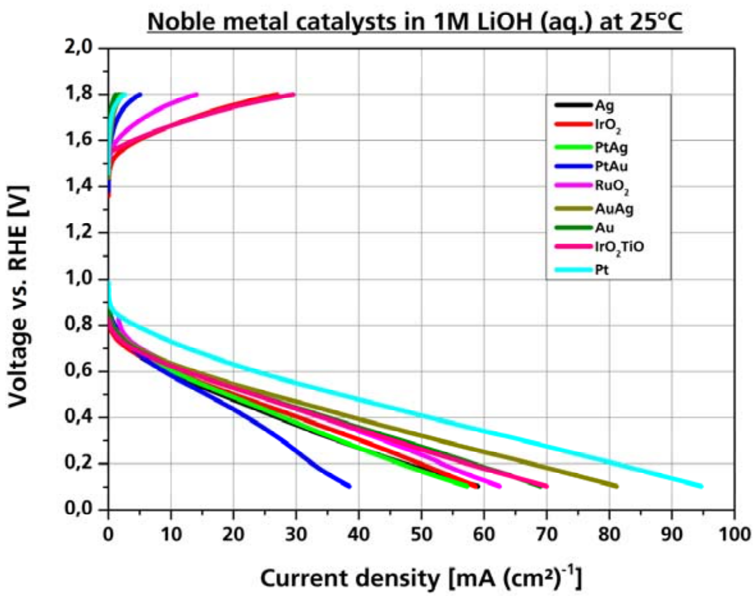
Oxide catalyst configuration

100 wt % catalyst



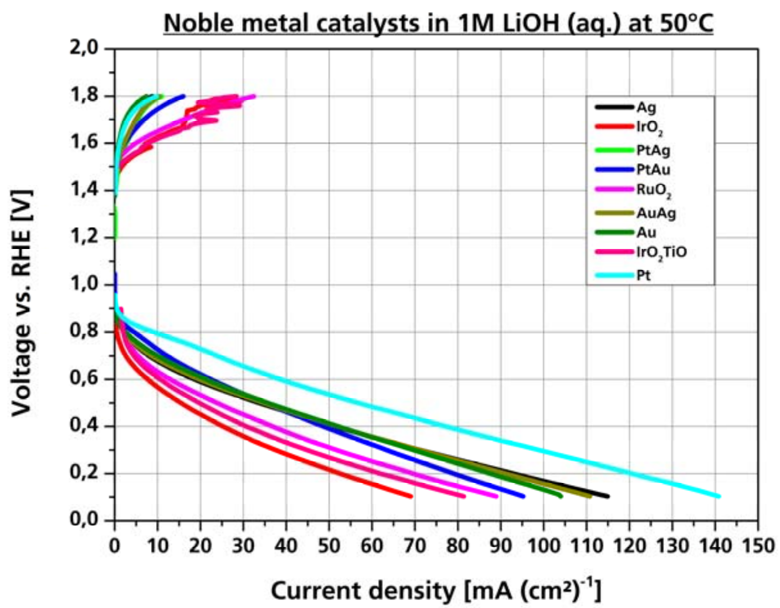
Electrode + Sigracet® GDL35 DC

Experimental results



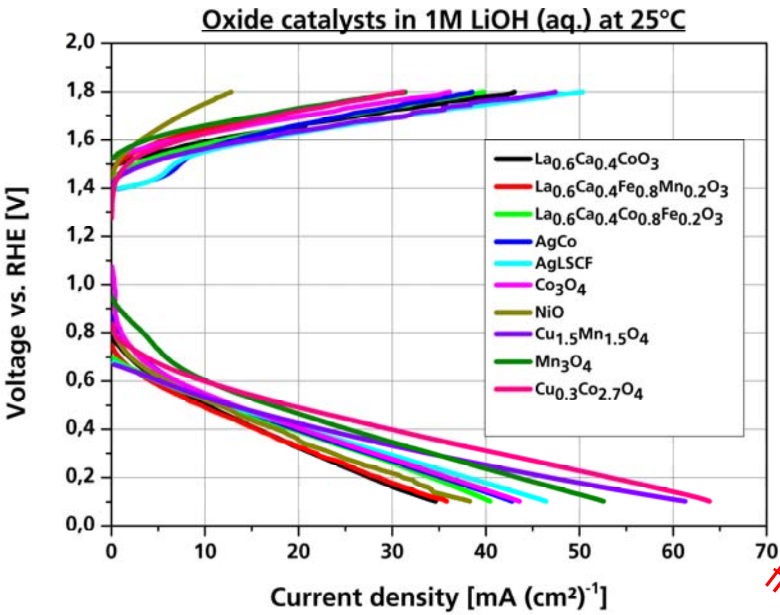
- Polarization curves with 1mV s^{-1}
- **Noble metal catalysts** show good activity towards oxygen reduction reaction (ORR) but poor activity towards oxygen evolution reaction (OER)

Increasing temperature from 25° C to 50° C



- Increasing the temperature shows a significant improvment of activity

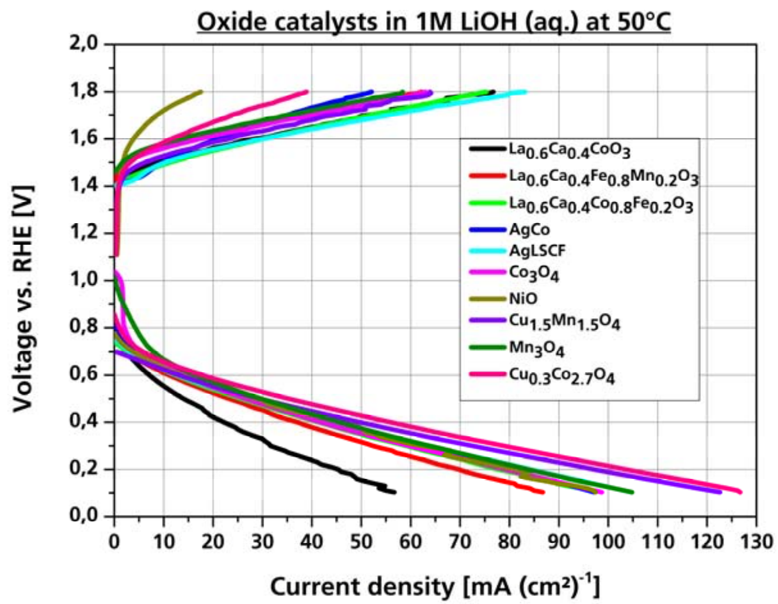
Experimental results



- Polarization curves with 1mV s^{-1}
- **Oxide catalysts** show more balanced characteristics towards ORR and OER than noble metal catalysts. Compared to their activity in ORR they show a high activity in OER.

Increasing temperature

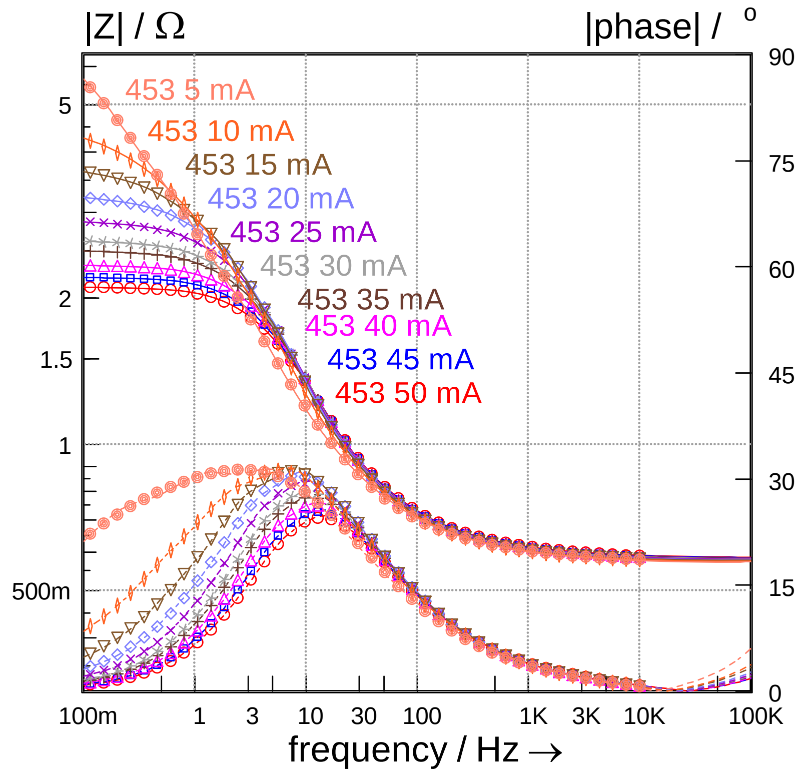
from 25° C to 50° C



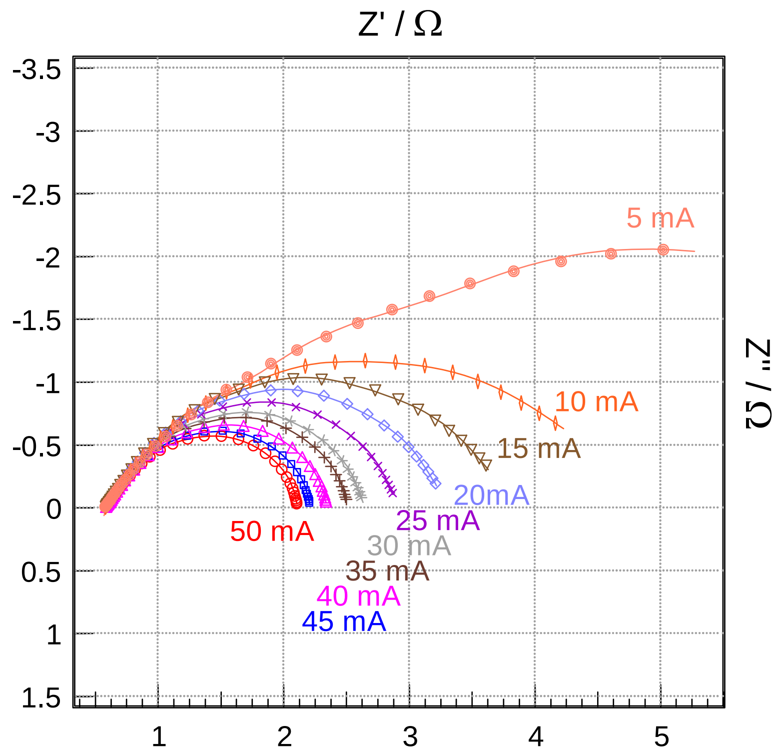
- Increasing the temperature shows a significant improvment of activity

DLR

Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i< -50 mAcm^{-2}



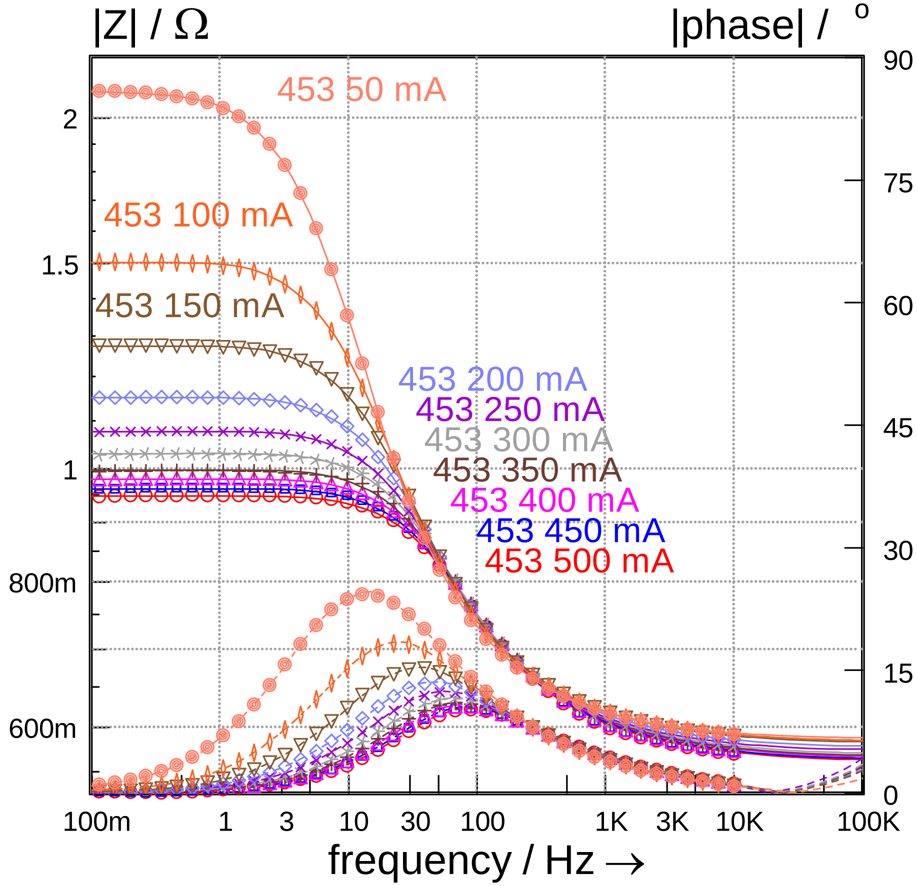
Bode representation

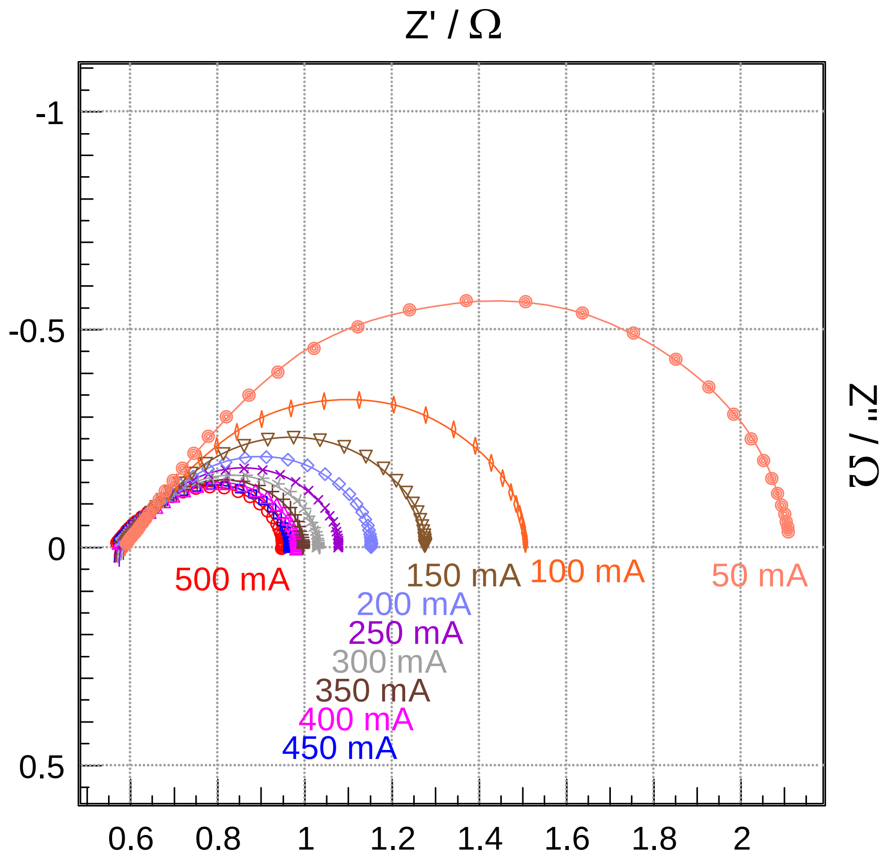


Nyquist representation

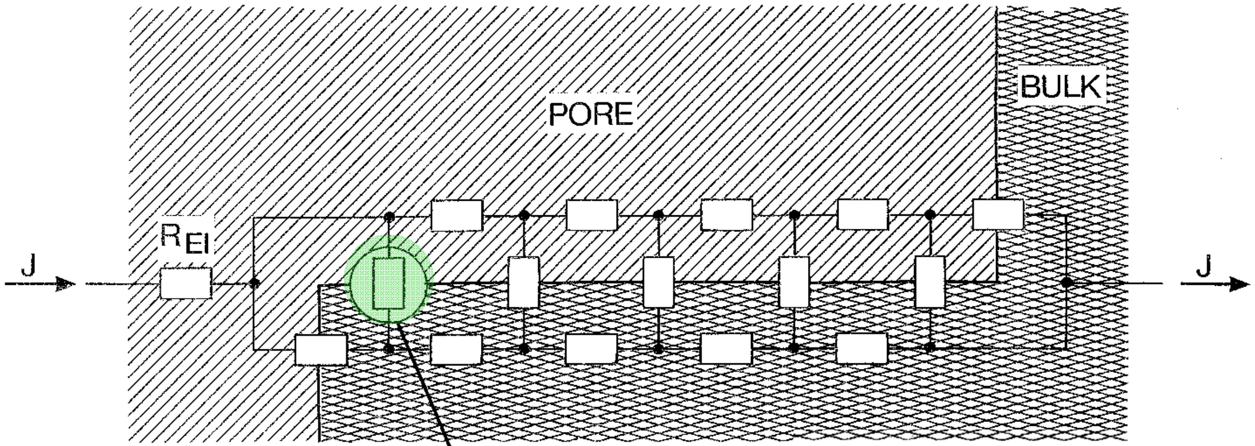
DLR

Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i> -50 mAcm^{-2}

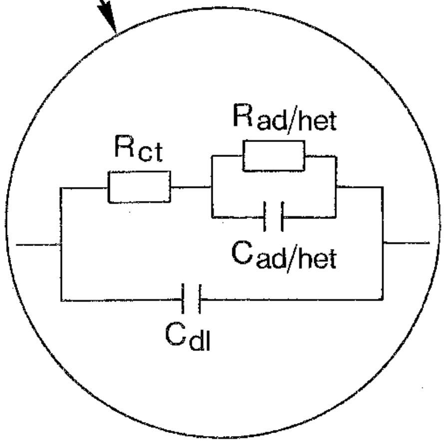


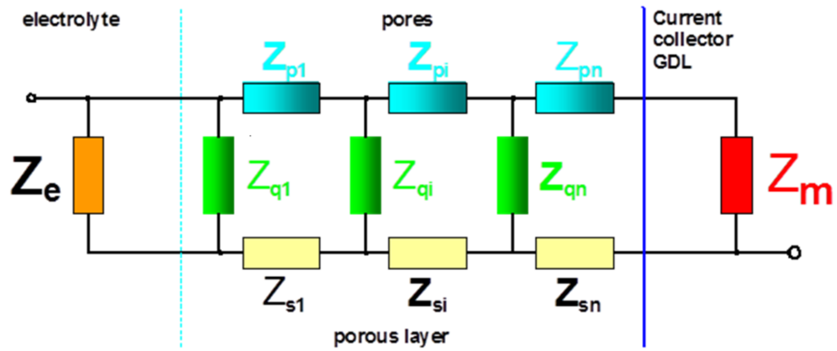


Electrode Model with cylindrical , homogeneous pores and complex Faraday-impedance

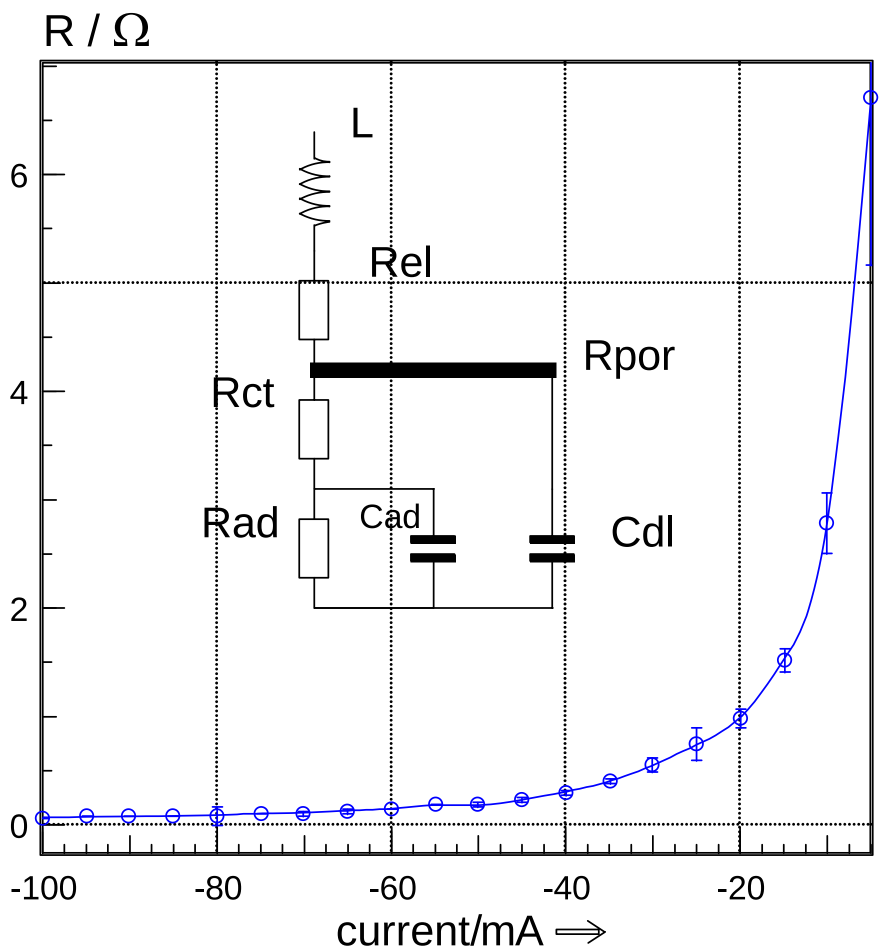


$Z_q=$

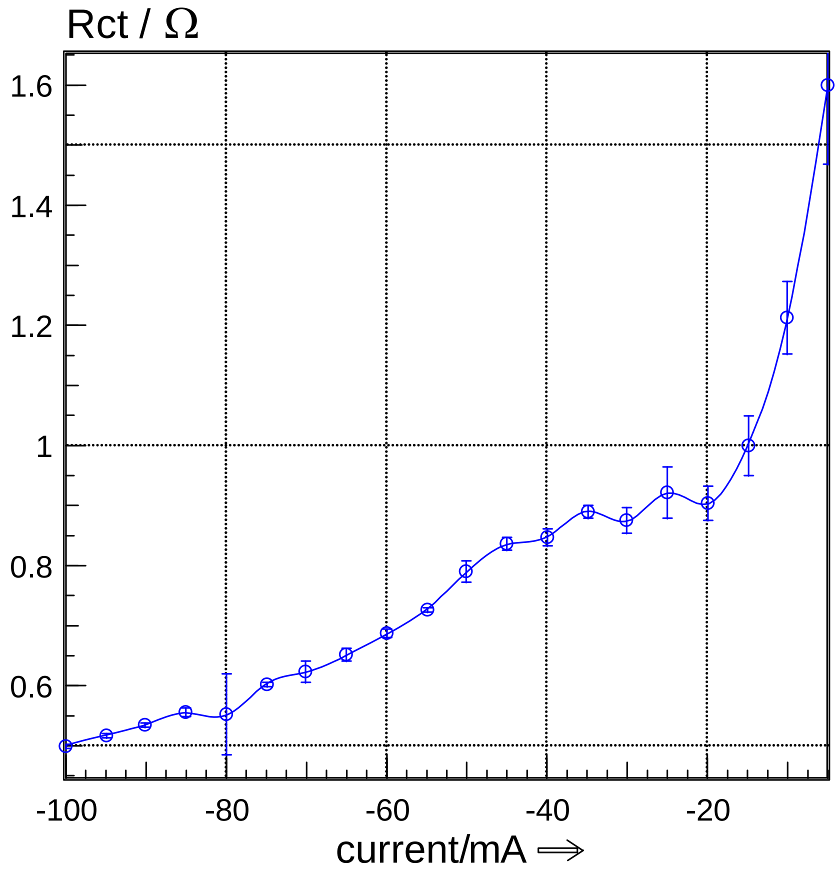




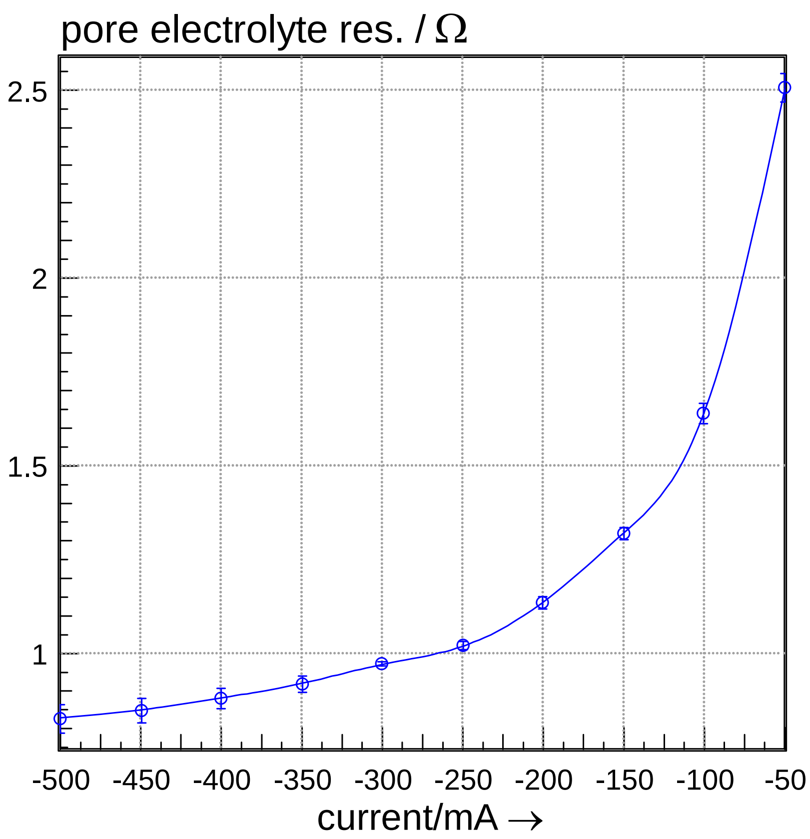
Evaluation of EIS measured during ORR Equivalent circuit and $R_{ad} = f(i)$



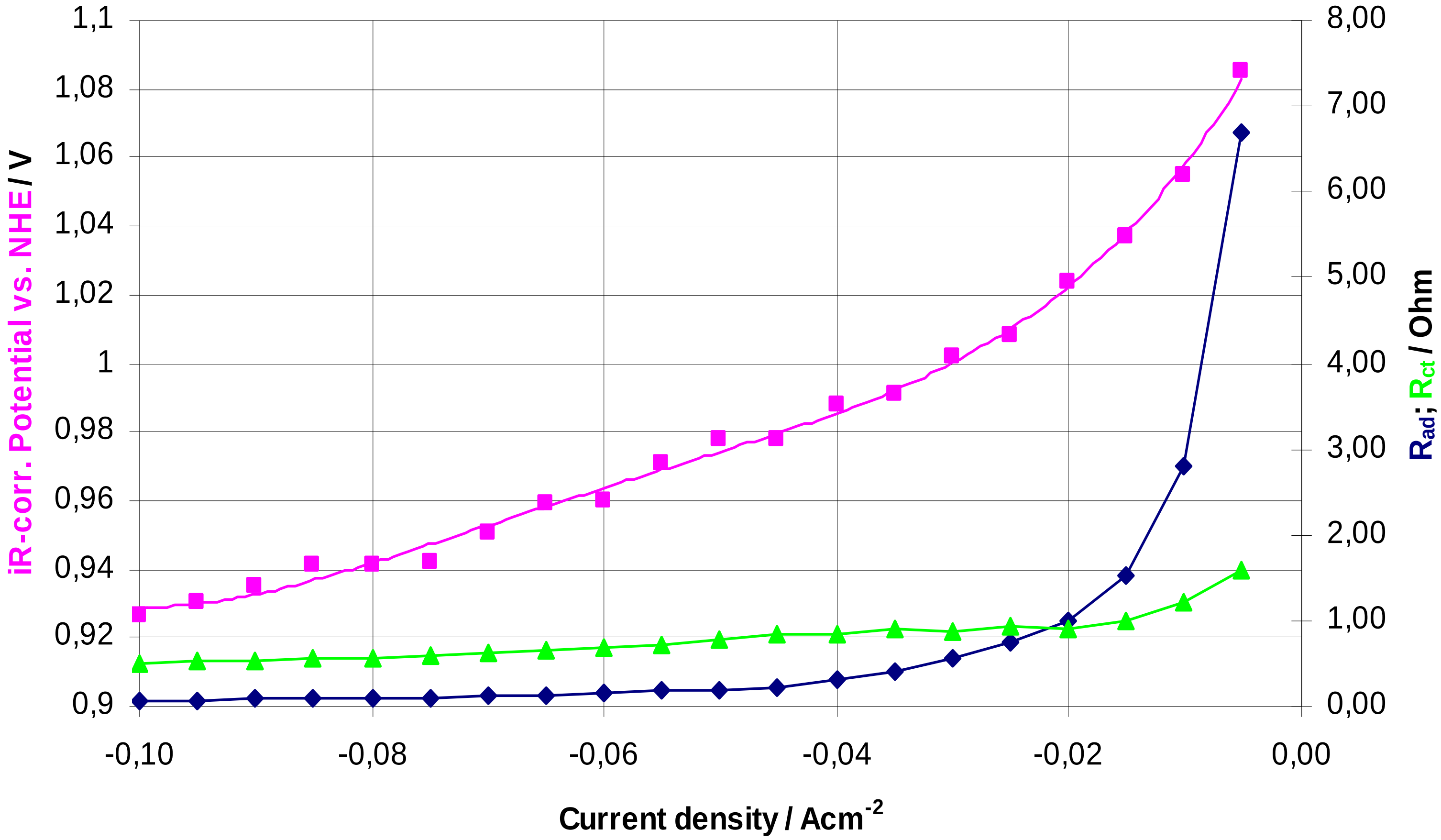
Current density dependency of the charge transfer resitance R_{ct}



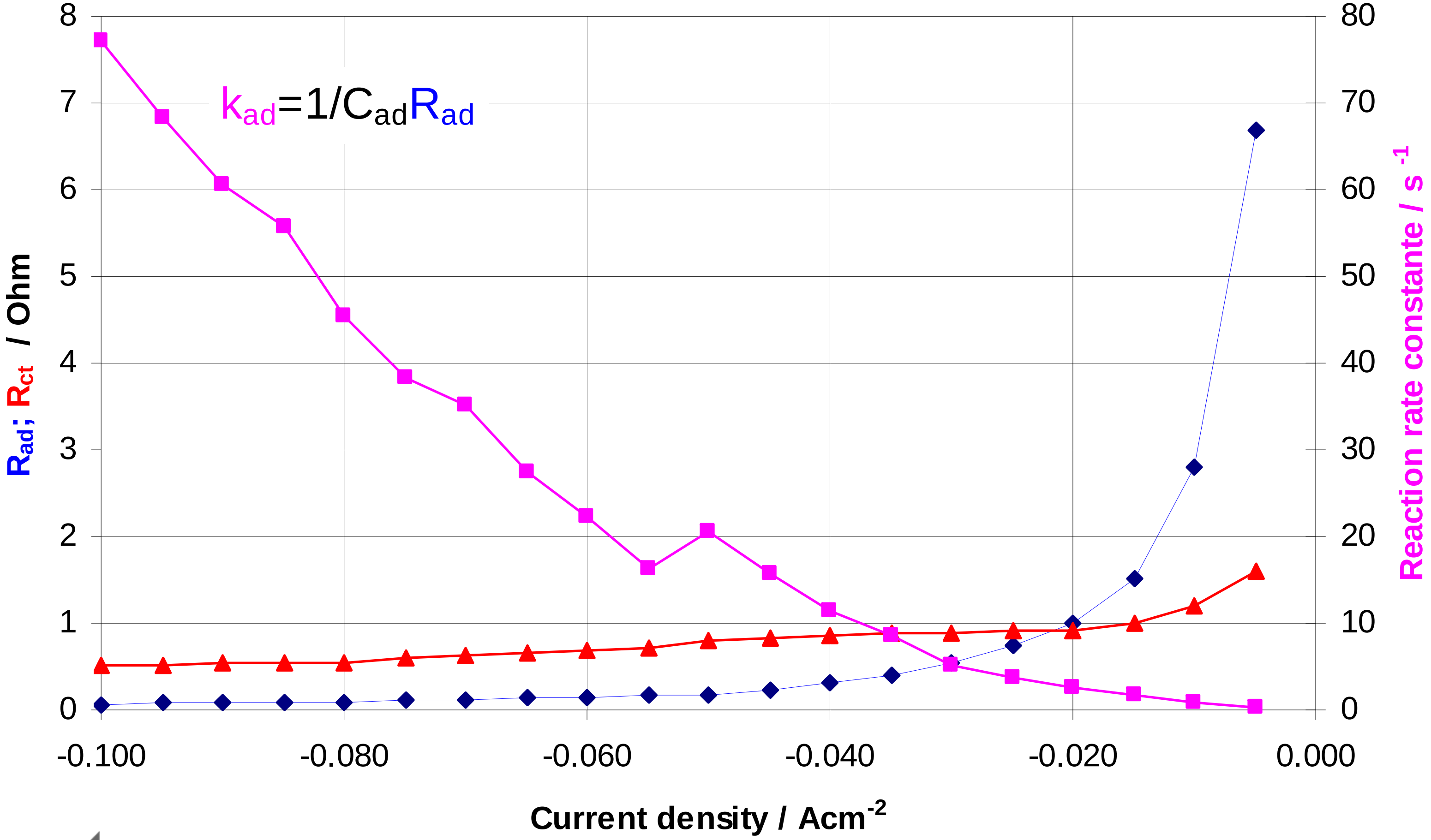
Current density dependency of electrolyte resistance inside the pore



U-i characteristic and current density dependency of impedance elements R_{ad} and R_{ct}

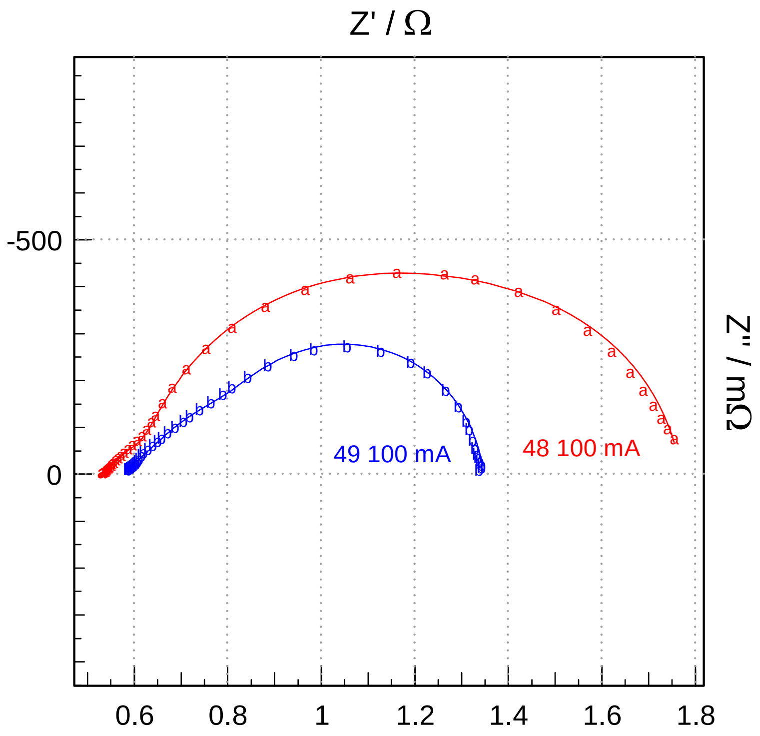


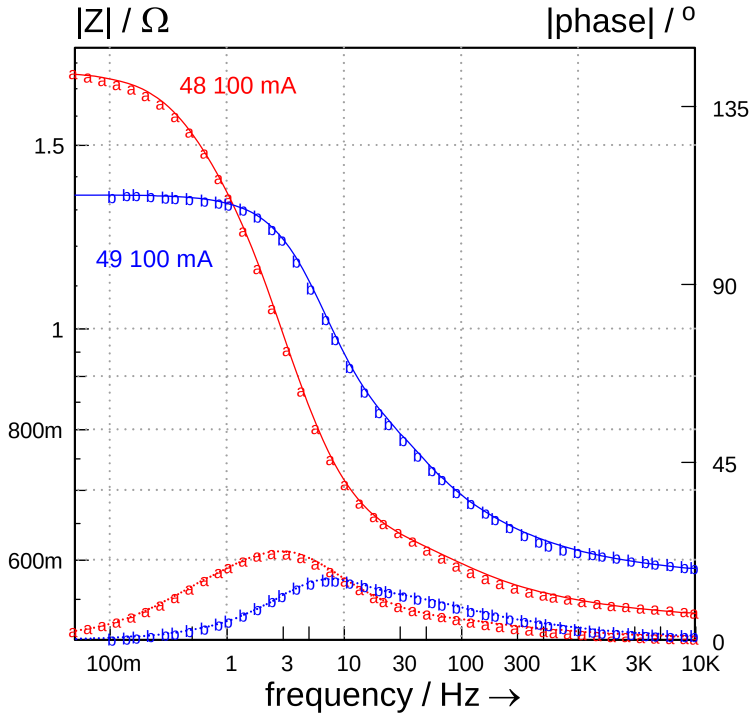
Current density dependency of k_{ad}, R_{ad} and R_{ct}, determined from EIS evaluation



DLR

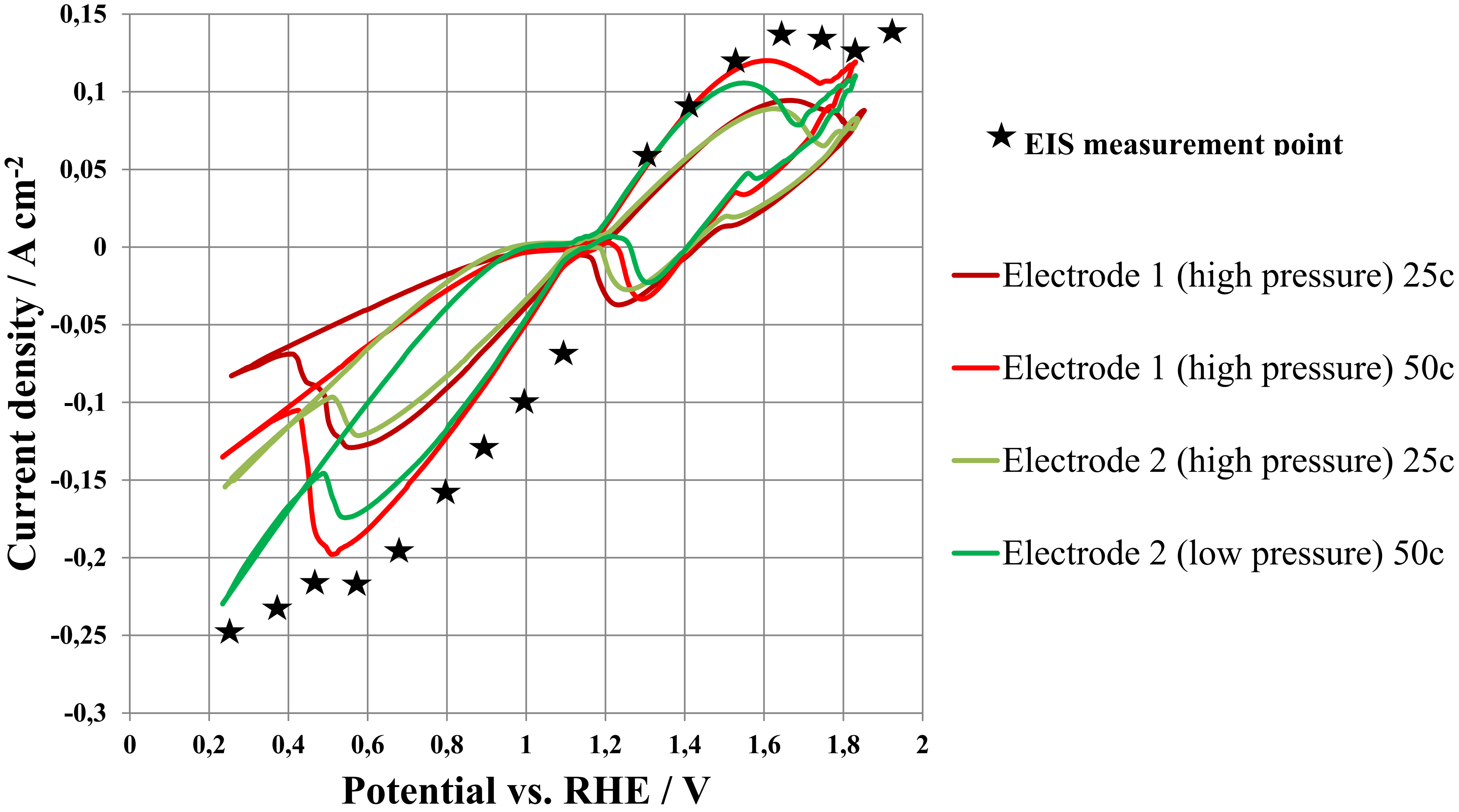
Influence of compacting pressure: Evaluation of EIS measured during OCR, 100 mA, 80°C, 10 N NaOH





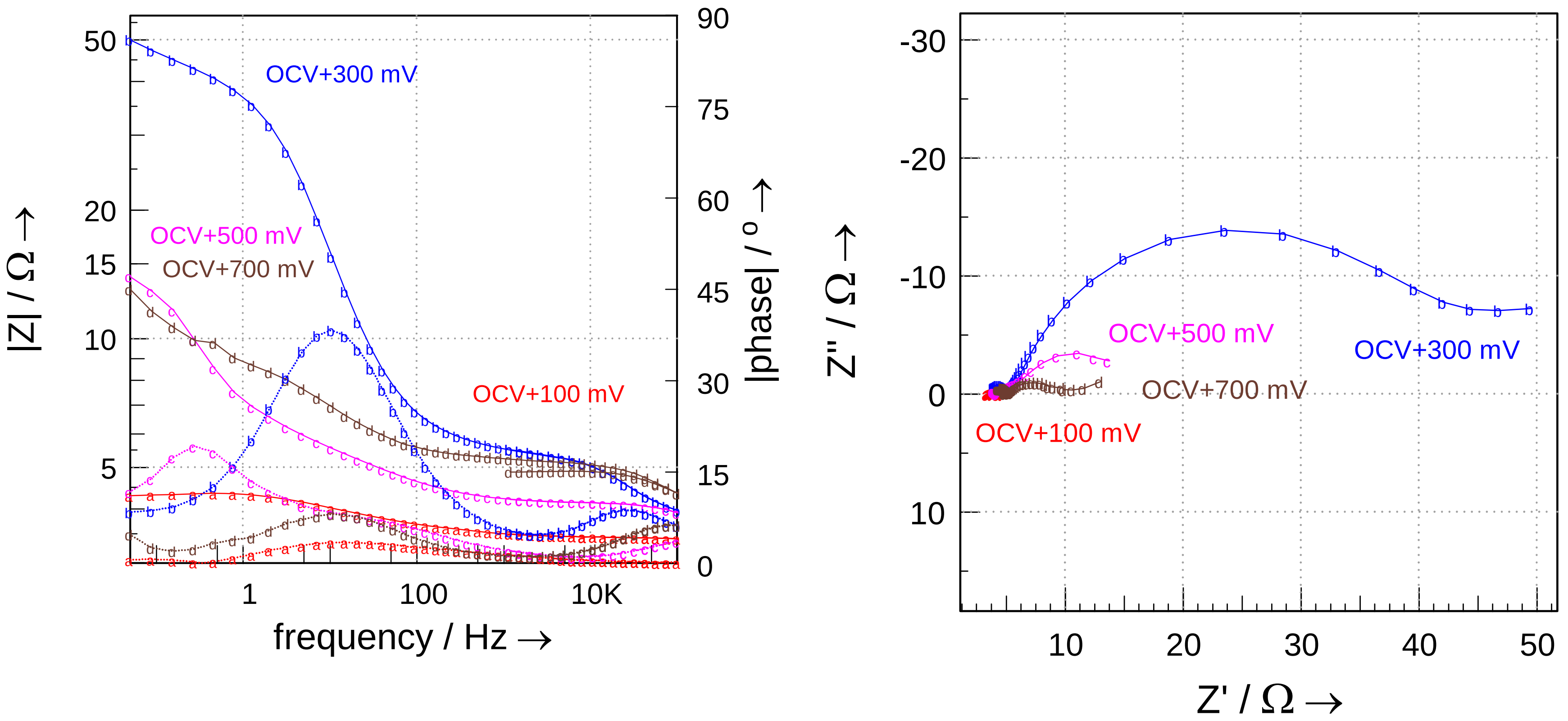
Sample	R_{ct}	R_{por}	R_{el}
48 (High pressure)	940Ω	287mΩ	524mΩ
49 (Low pressure)	534Ω	727mΩ	577mΩ

Overview EIS measurement points and CV with 1 mV/s at RT, 1 N LiOH , Ag-GDE



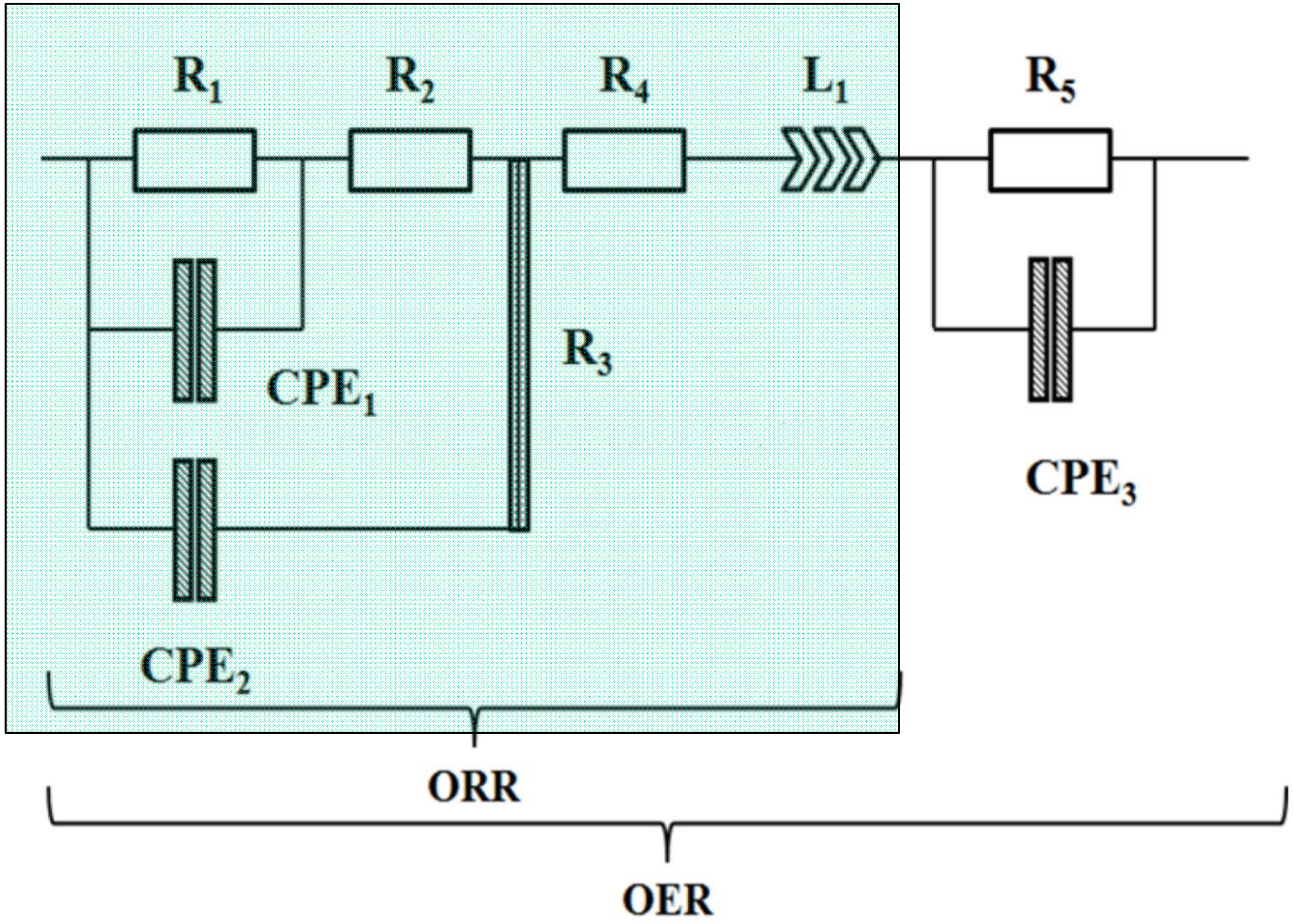
DLR

Impedance measurements during Oxygen evolution on Ag-GDE (high pressure), 1 N LiOH, 25° C



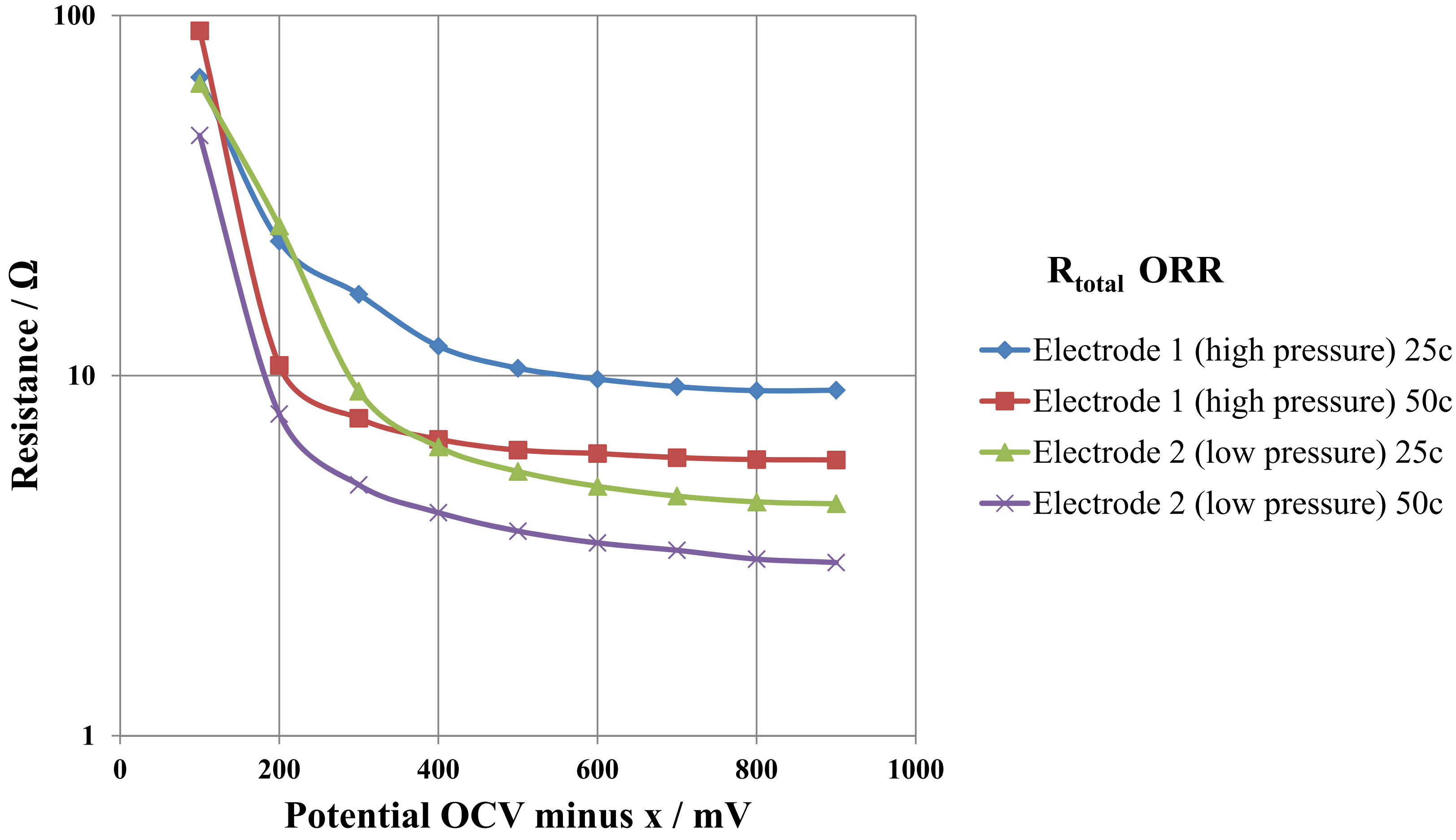
DLR

Equivalent circuit used for evaluation of EIS during OCR and OER at different electrodes for Lithium-Air batteries

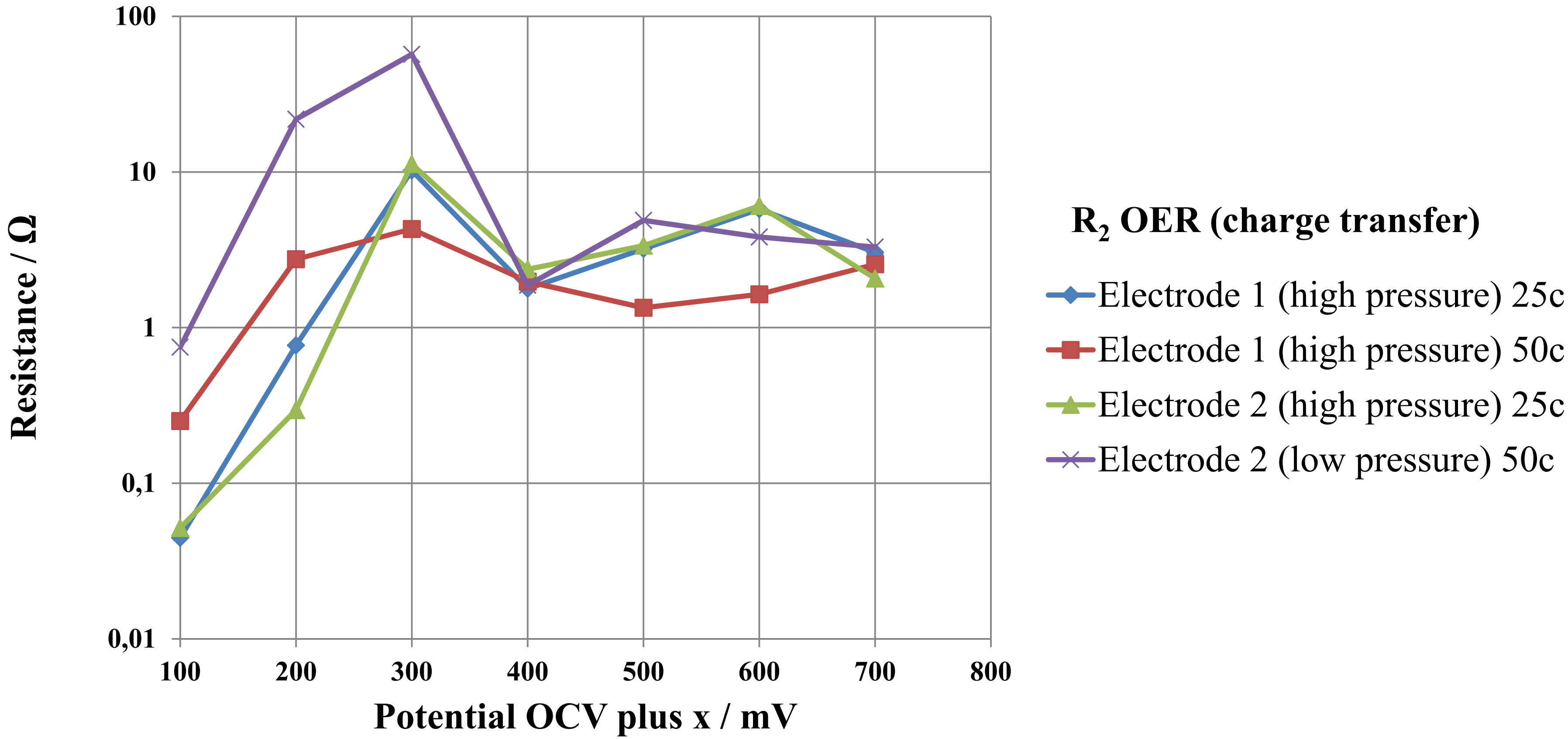


DLR

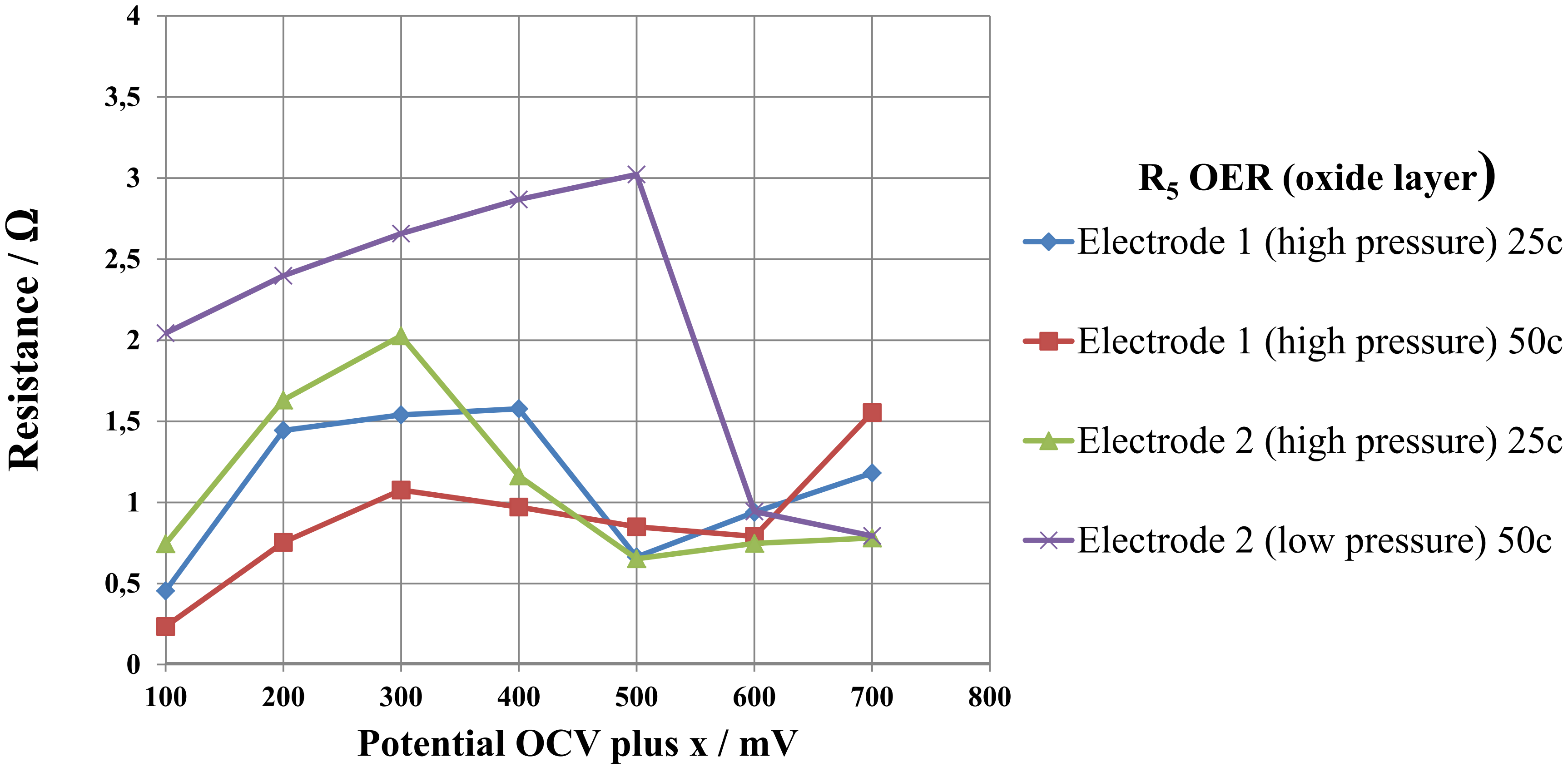
Potential dependency of total resistance during ORR at different electrodes, 1 N LiOH



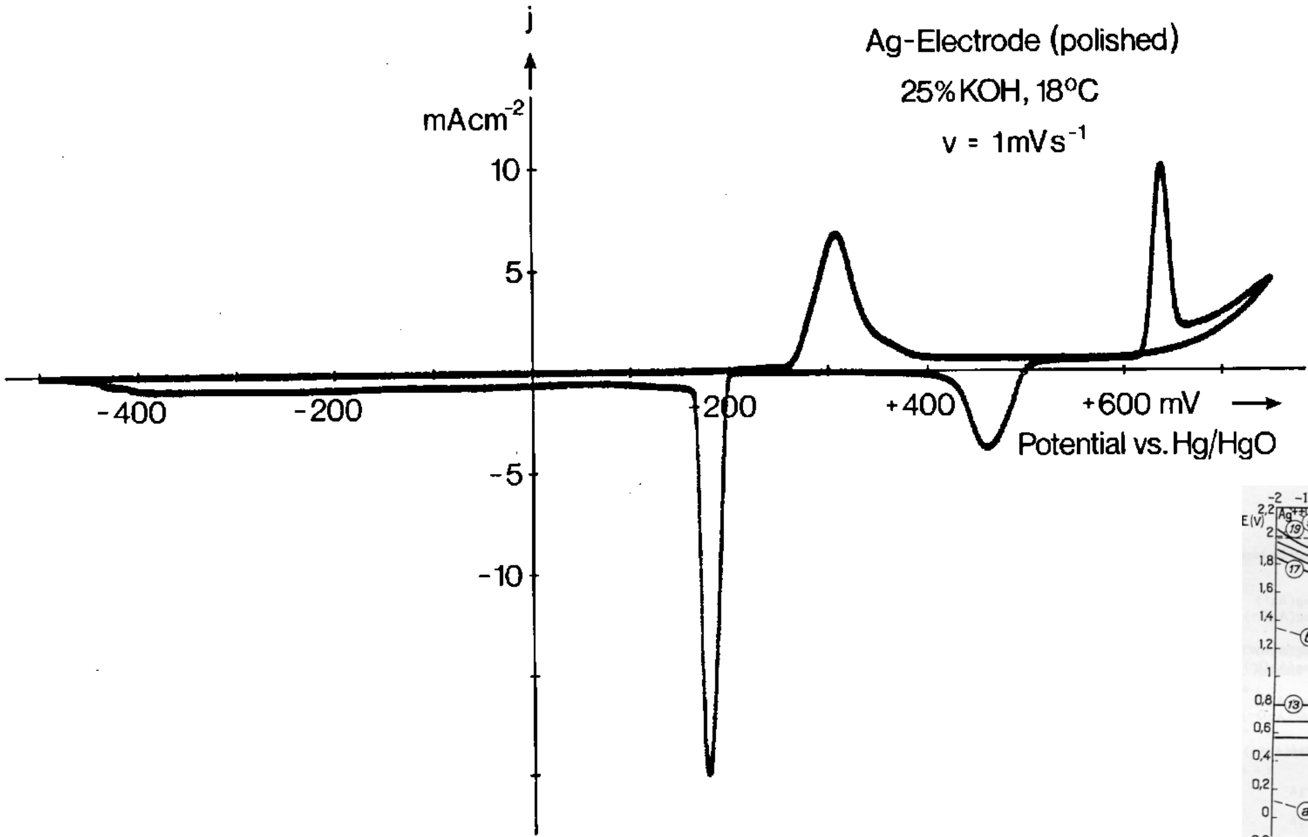
Potential dependency of charge transfer resistance during OER



Potential dependency of charge transfer resistance in oxide layer potential region (OER)



CV of a polished Ag electrode, 25% KOH, O_2 sat.



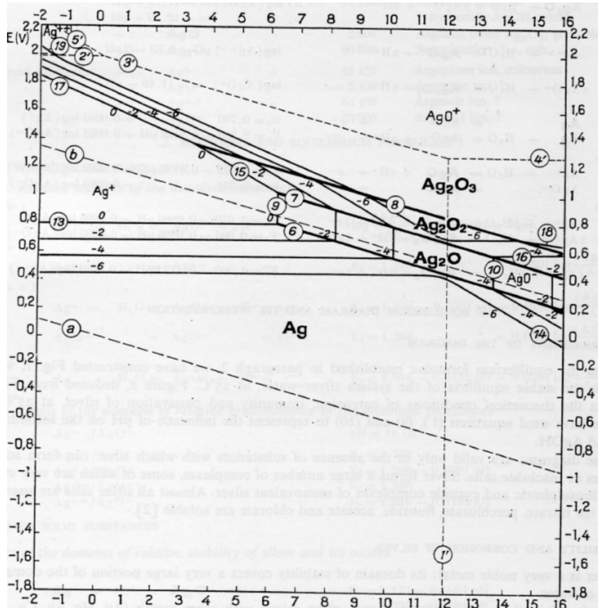
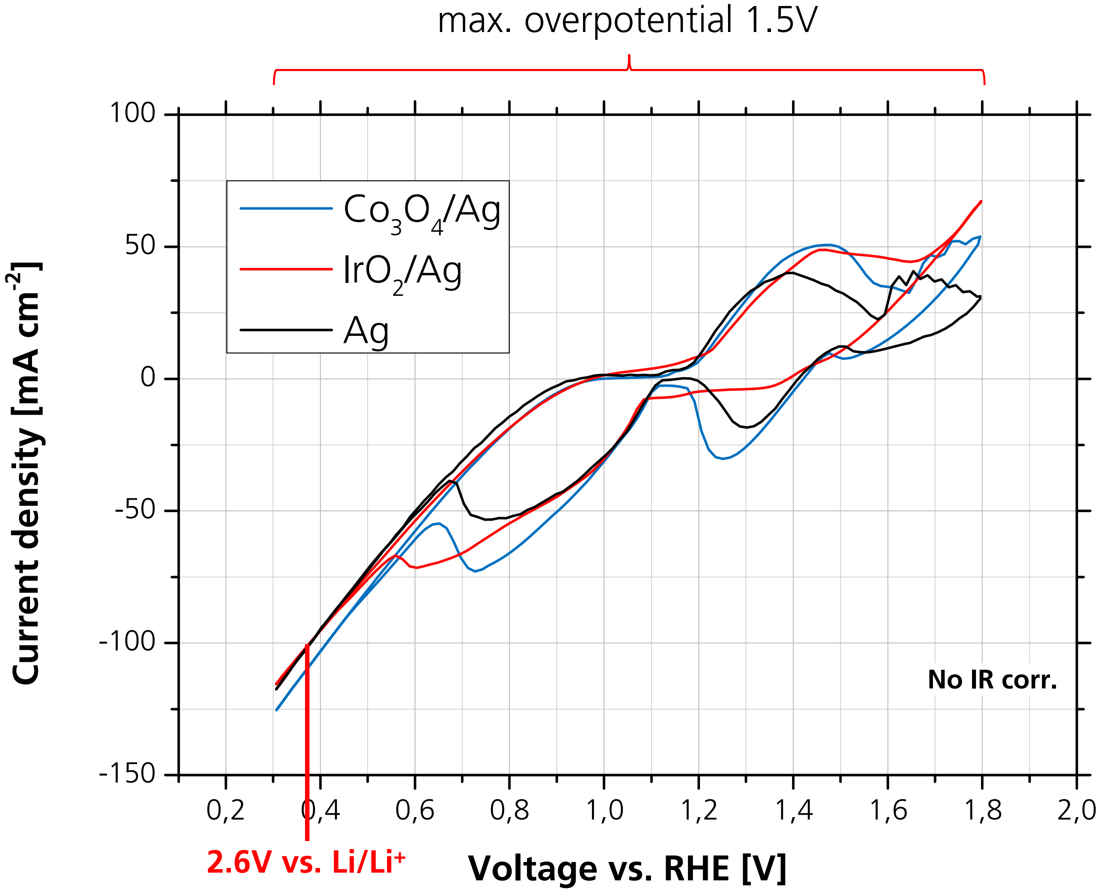


Fig. 1. Potential–pH equilibrium diagram for the system silver–water, at 25°C.

Bi-functional Oxygen-Electrodes: IrO_2/- and Co_3O_4/Ag-electrodes

- CV´s electrodes 20 wt. % catalyst (IrO_2, Co_3O_4
- Improved cycling performance due to use of IrO_2 and Co_3O_4 compared to pure Ag

Current density @ 2.6V vs. Li/Li+ [mA cm^{-2}]	
IrO_2/Ag	99,7
Co_3O_4/Ag	107



N. Wagner et al., German Patent Application, 2014

Conclusion

- From the catalyst screening, a new bifunctionall catalysts system for the cathode of a Li-air battery was found
- From the evaluation of the measured impedance spectra one can propose a reaction mechanism for the ORR:
  - Adsorptions- / heterogeneous reactions and charge transfer reaction are consecutive reactions
  - Reaction mechanism and rate determining step is changing at higher current densities at ca. 20 $mAcm^{-2}$
  - Production parameters, composition and structure have a strong influence on electrode reactivity
  - Change of reaction zone with current density
- Silver electrodes are not stable during OER

Thank you for your Attention !

Acknowledgment

Bundesministerium für Bildung und Forschung

luft li

Reactions pathways for the cathodic oxygen reduction in alkaline solution

Direct-X 4e$^-$ - path: **$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$**

$O_2 + 2M \leftrightarrow 2M\ldots O$

$2\,(M\ldots O + e^- \rightarrow MO^-)$

$2\,(MO^- + H_2O \leftrightarrow MOH + OH^-)$

$2\,(MOH + e^- \leftrightarrow OH^- + M)$

Peroxid - Path: **$H_2O + O_2 + 2e^- \leftrightarrow HO_2^- + OH^-$**

$O_2 + M \leftrightarrow M\ldots O_2$

$M\ldots O_2 + e^- \rightarrow MO_2^-$

$MO_2^- + H_2O \leftrightarrow MHO_2 + OH^-$

$MHO_2 + e^- \leftrightarrow HO_2^- + M$

Peroxid-Reduction: **$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$**

$HO_2^- + M \leftrightarrow MHO_2^-$

$MHO_2^- + H_2O \leftrightarrow MH_2O_2 + OH^-$

$MH_2O_2 + e^- \rightarrow MOH + OH^-$

$MOH + e^- \leftrightarrow M + OH^-$

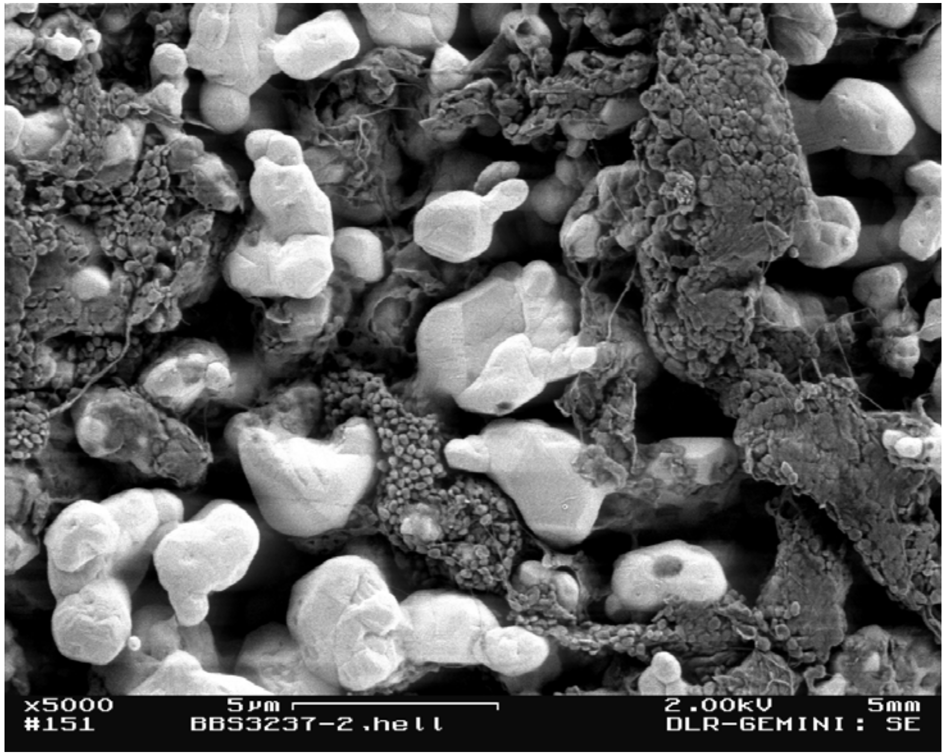
Catalytically Peroxid-decomposition: **$2HO_2^- \rightarrow O_2 + 2OH^-$**

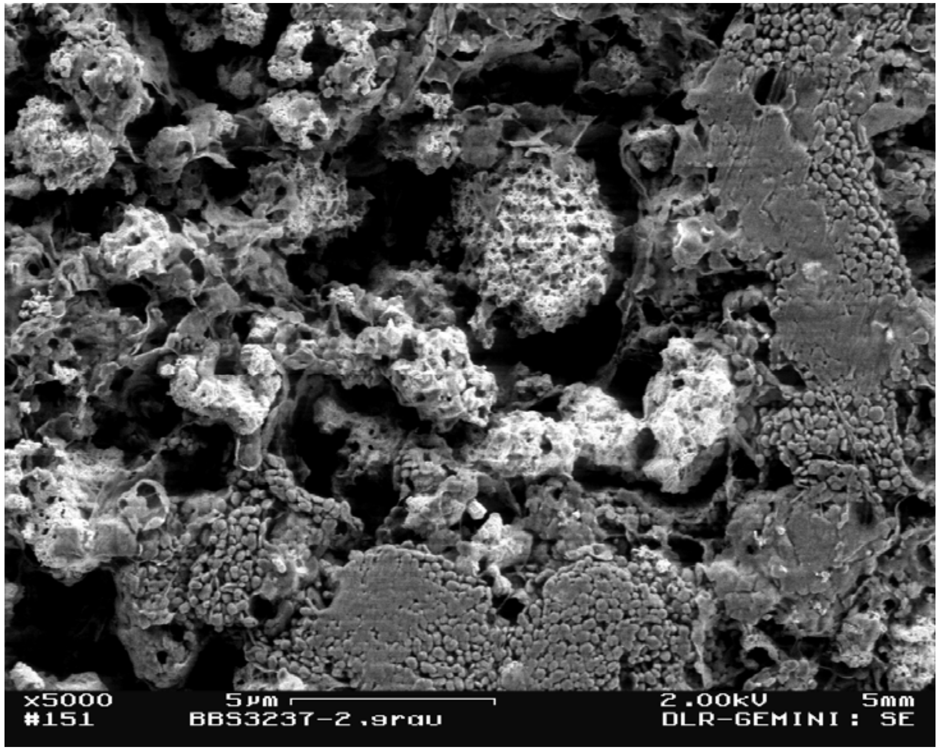
$HO_2^- + M \leftrightarrow MHO_2^-$

$MHO_2^- \rightarrow MO + OH^-$

$MO + HO_2^- \rightarrow O_2 + OH^- + M$

SEM pictures of Ag-GDE, produced by the RMR technique (Ag_2O+PTFE)





Ag-GDE, unused part

Ag-GDE, used